

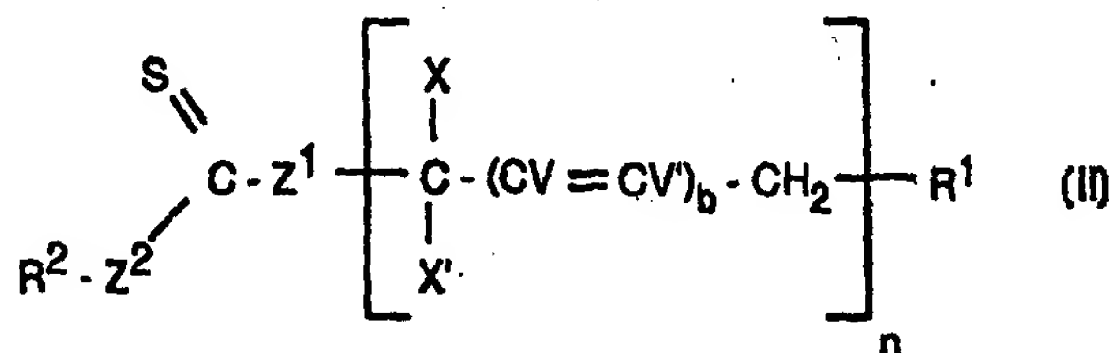
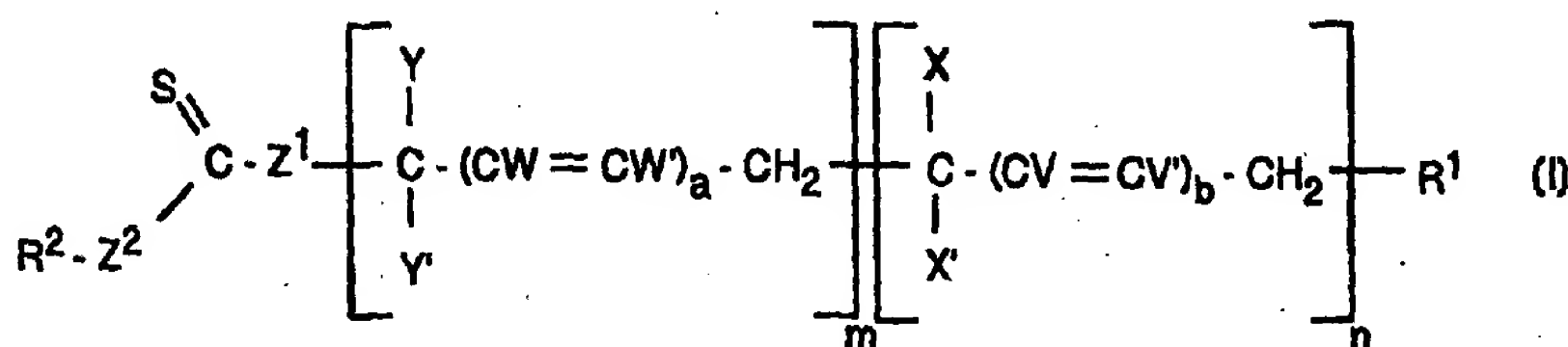


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(21) Numéro de la demande internationale: PCT/FR98/01316 (22) Date de dépôt international: 23 juin 1998 (23.06.98) (30) Données relatives à la priorité: 97/07764 23 juin 1997 (23.06.97) FR (71) Déposant (pour tous les Etats désignés sauf US): RHO- DIA CHIMIE [FR/FR]; 25, quai Paul Doumer, F-92408 Courbevoie Cedex (FR). (72) Inventeurs; et (75) Inventeurs/Déposants (US seulement): CORPART, Pascale [FR/FR]; 3, allée des Erables, F-95110 Sannois (FR). CHARMOT, Dominique [FR/FR]; 10, rue Colette Audry, F-93310 Le Pré Saint Gervais (FR). BIADATTI, Thibaud [FR/FR]; 2, chemin du Bois d'Opio, F-06650 Opio (FR). ZARD, Samir [FR/FR]; 6, impasse des 4 Vents, F-91190 Gif sur Yvette (FR). MICHELET, Daniel [FR/FR]; Résidence Parc d'Alco, 119, rue Michel Teule, F-34080 Montpellier (FR). (74) Mandataire: DUBRUC, Philippe; Rhodia Services, Propriété Industrielle, 25, quai Paul Doumer, F-92408 Courbevoie Cedex (FR).	(81) Etats désignés: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, brevet ARIPO (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), brevet eurasién (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), brevet européen (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), brevet OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Publiée Avec rapport de recherche internationale. Avant l'expiration du délai prévu pour la modification des revendications, sera republiée si des modifications sont reçues.	

(54) Title: METHOD FOR BLOCK POLYMER SYNTHESIS BY CONTROLLED RADICAL POLYMERISATION

(54) Titre: PROCEDE DE SYNTHÈSE DE POLYMERES A BLOCS PAR POLYMERISATION RADICALE CONTROLEE



(57) Abstract

The invention concerns a method for polymerising block polymers of general formula (I) which consists in contacting: an ethylenically unsaturated monomer of formula: $CYY' (=CW - CW')_a = CH_2$; a precursor compound of general formula (II); a radical polymerisation catalyst.

(57) Abrégé

L'invention concerne un procédé de polymérisation de polymères à blocs de formule générale (I), procédé dans lequel on met en contact: un monomère éthyléniquement insaturé de formule: $CYY' (=CW - CW')_a = CH_2$; un composé précurseur de formule générale (II); un initiateur de polymérisation radicalaire.

**PROCEDE DE SYNTHESE DE POLYMERES A BLOCS
PAR POLYMERISATION RADICALAIRE CONTROLEE**

La présente invention concerne un nouveau procédé de polymérisation radicalaire
5 donnant accès à des copolymères à blocs.

Les polymères à blocs sont habituellement préparés par polymérisation ionique.
Ce type de polymérisation présente l'inconvénient de ne permettre la polymérisation que
de certains types de monomères apolaires, notamment le styrène et le butadiène, et de
10 requérir un milieu réactionnel particulièrement pur et des températures souvent
inférieures à l'ambiante de manière à minimiser les réactions parasites, d'où des
contraintes de mise en oeuvre sévères.

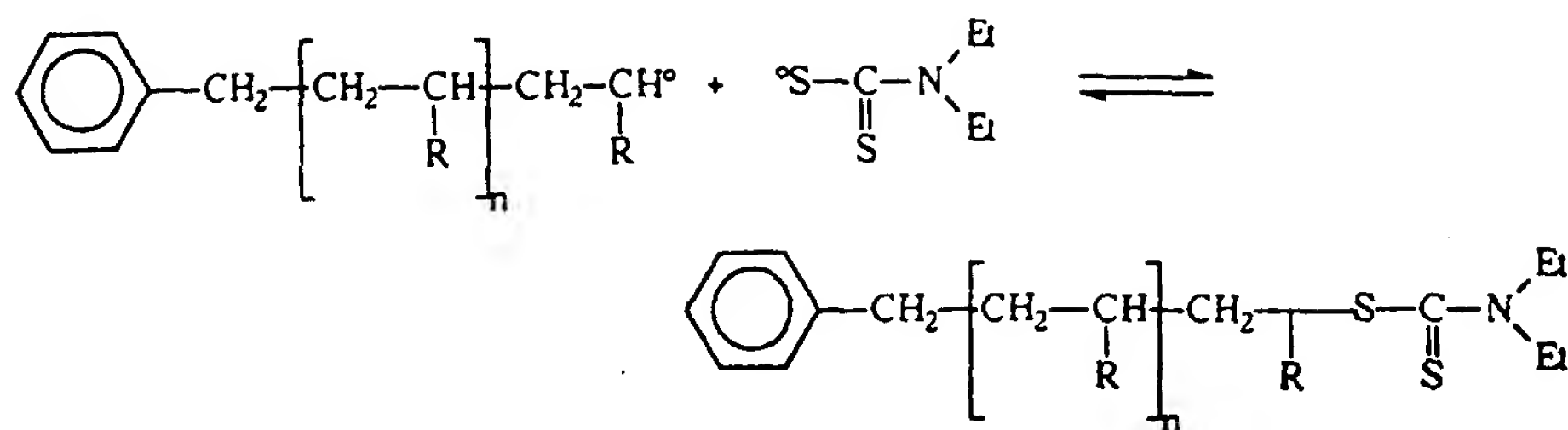
La polymérisation radicalaire présente l'avantage d'être mise en oeuvre facilement
15 sans que des conditions de pureté excessives soient respectées et à des températures
égales ou supérieures à l'ambiante. Cependant, jusqu'à récemment il n'existait pas de
procédé de polymérisation radicalaire permettant d'obtenir des polymères à blocs.

Depuis, un nouveau procédé de polymérisation radicalaire s'est développé : il
20 s'agit de la polymérisation radicalaire dite "contrôlée" ou "vivante". La polymérisation
radicalaire contrôlée procède par croissance par propapagation de macroradicaux. Ces
macroradicaux, dotés d'un temps de vie très faible, se recombinent de façon irréversible
par couplage ou dismutation. Lorsque la polymérisation se déroule en présence de
plusieurs comonomères, la variation de composition du mélange est infiniment faible
25 devant le temps de vie du macroradical de sorte que les chaînes présentent un
enchaînement des unités monomères statistique et non un enchaînement séquencé.

Récemment des techniques de polymérisation radicalaire contrôlée ont été mises
au point, dans lesquelles les extrémités de chaînes de polymères peuvent être
réactivées sous forme de radical par scission homolytique de liaison (par exemple C-O,
30 ou C-Halogène).

La polymérisation radicalaire contrôlée présente donc les aspects distinctifs
suivants :

1. le nombre de chaînes est fixe pendant toute la durée de la réaction,
- 35 2. les chaînes croissent toutes à la même vitesse, ce qui se traduit par :
 - une augmentation linéaire des masses moléculaires avec la conversion,
 - une distribution des masses resserrée,



Le principe repose sur la photolyse de la liaison C-S qui régénère le macroradical carboné, d'une part, et le radical dithiocarbamyl, d'autre part. Le caractère contrôlé de la réaction est dû à la réversibilité de la liaison C-S sous irradiation UV. Il est ainsi possible d'obtenir des copolymères à blocs. En revanche la constante d'équilibre de la réaction 1 ci-dessus n'est pas très grande par rapport à la vitesse de propagation ce qui a pour conséquence de générer des distributions en masses moléculaires relativement larges. Ainsi, l'indice de dispersion ($Id = M_w/M_n$) est compris entre 2 et 5 (Otsu *et al.*, 25,7/8,643-650,(1989)).

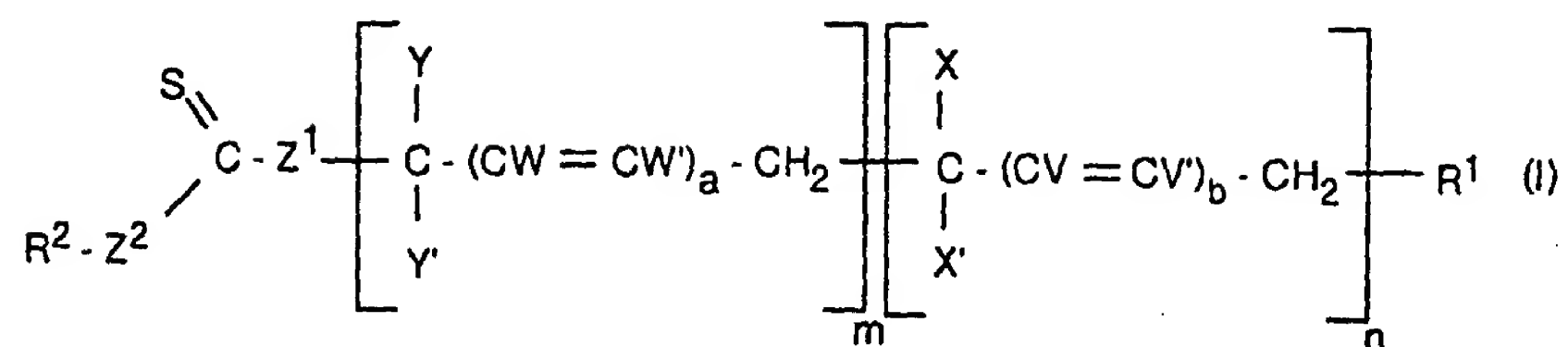
Les disulfures de xanthates et de dithiocarbamates sont eux-mêmes bien connus comme agents de transferts en polymérisation radicalaire conventionnelle en mode thermique et en présence d'amorceur, mais aucun n'a permis à ce jour de contrôler la polymérisation, encore moins de produire des copolymères à blocs.

Jusqu'à présent il était connu que les disulfures (tetra-alkylthiurame disulfure, diisopropylxanthate disulfure, mercaptobenzothiazole disulfure) étaient activables thermiquement ou sous irradiation UV, alors que les monosulfures (dithiocarbamates, xanthates substitués) étaient activables uniquement sous irradiation UV (Roha *et al.*, 20 *Macromol. Symp.*, 91, 81-92, (1995), Okawara *et al.*, Bull. of the Tokyo Inst. of Techn., n° 78, 1966).

La polymérisation radicalaire contrôlée faisant appel à une source d'irradiation UV est cependant très difficile à mettre en œuvre, particulièrement d'un point de vue industriel, car la pénétration des photons UV dans le milieu de polymérisation est limitée, tant par des phénomènes d'absorption (la plupart des monomères éthyléniques adsorbent dans la plage 210-280 nm), que par les phénomènes de diffusion dans les milieux dispersés (suspension, émulsion).

D'autre part, il a été montré (Turner *et al.*, *Macromolecules*, 23,1856-1859, (1990)) que la photopolymérisation en présence de dithiocarbamate génère du disulfure carbone et peut s'accompagner d'une perte de contrôle de la polymérisation.

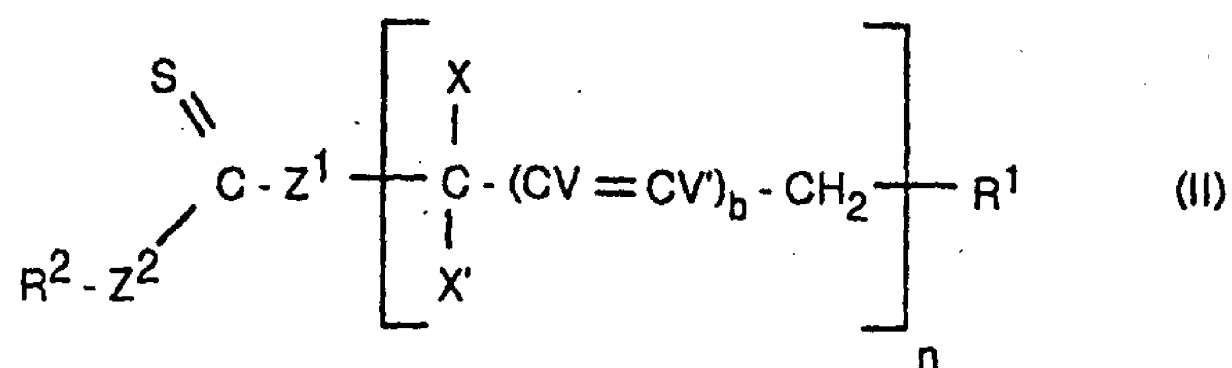
Pour ces raisons, on cherche donc à développer une technique permettant d'accéder à des copolymères à blocs par un procédé sans irradiation UV, de préférence



dans lequel on met en contact :

- un monomère éthyléniquement insaturé de formule : $CYY' (= CW - CW')_a = CH_2$,
- un composé précurseur de formule générale (II) :

5



- un initiateur de polymérisation radicalaire.

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L'invention concerne également les polymères à blocs susceptible d'être obtenus par le procédé ci-dessus.

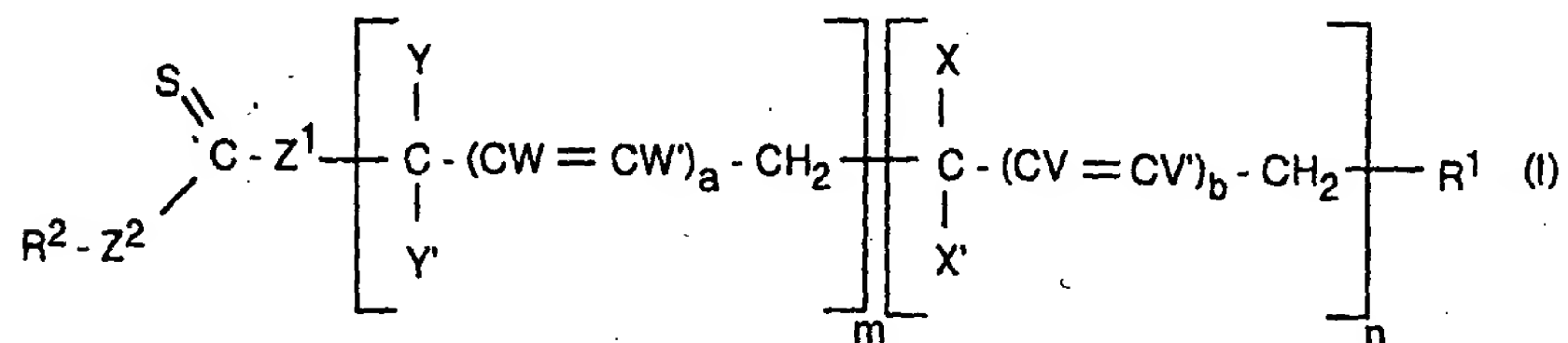
Enfin, l'invention concerne des polymères de formule générale (II) dont l'indice de polydispersité est d'au plus 2.

15

D'autres détails et avantages de l'invention apparaîtront plus clairement à la lecture de la description et des exemples.

L'invention concerne donc tout d'abord un procédé de polymérisation de polymères à blocs de formule générale (I) :

20



dans laquelle :

- $Z^1 = S$ ou P ,
- $Z^2 = O$, S ou P ,
- R^1 et R^2 , identiques ou différents, représentent :

25

Le procédé consiste donc à mettre en contact un initiateur de polymérisation radicalaire, un monomère éthyléniquement insaturé et un précurseur de formule générale (II).

5 **L'initiateur de polymérisation radicalaire** peut être choisi parmi les initiateurs classiquement utilisés en polymérisation radicalaire. Il peut s'agir par exemple d'un des initiateurs suivants :

- les peroxydes d'hydrogène tels que : l'hydroperoxyde de butyle tertiaire, l'hydroperoxyde de cumène, le t-butyl-peroxyacétate, le t-butylperoxybenzoate, le t-butylperoxyoctoate, le t-butylperoxynéodécanoate, le t-butylperoxyisobutarate, le peroxyde de lauroyle, le t-amylperoxypivalte, le t-butylperoxypivalate, le peroxyde de dicumyl, le peroxyde de benzoyle, le persulfate de potassium, le persulfate d'ammonium,

10 - les composés azoïques tels que : le 2,2'-azobis(isobutyronitrile), le 2,2'-azobis(2-butanenitrile), le 4,4'-azobis(4-acide pentanoïque), le 1,1'-azobis(cyclohexane-carbonitrile), le 2-(t-butylazo)-2-cyanopropane, le 2,2'-azobis[2-méthyl-N-(1,1)-bis(hydroxyméthyl)-2-hydroxyéthyl] propionamide, le 2,2'-azobis(2-méthyl-N-hydroxyéthyl)-propionamide, le dichlorure de 2,2'-azobis(N,N'-diméthylèneisobutyramidine), le dichlorure de 2,2'-azobis (2-amidinopropane), le 2,2'-azobis (N,N'-diméthylèneisobutyramide), le 2,2'-azobis(2-méthyl-N-[1,1-bis(hydroxyméthyl)-2-hydroxyéthyl] propionamide), le 2,2'-azobis(2-méthyl-N-[1,1-bis(hydroxyméthyl)éthyl] propionamide), le 2,2'-azobis[2-méthyl-N-(2-hydroxyéthyl) propionamide], le 2,2'-azobis(isobutyramide) dihydrate,

25 - les systèmes redox comportant des combinaisons telles que :
- les mélanges de peroxyde d'hydrogène, d'alkyle, peresters, percarbonates et similaires et de n'importe lequel des sels de fer, de sels titaneux, formaldéhyde sulfoxyate de zinc ou formaldéhyde sulfoxyate de sodium, et des sucres réducteurs,
- les persulfates, perborate ou perchlorate de métaux alcalins ou d'ammonium en association avec un bisulfite de métal alcalin, tel que le métabisulfite de sodium, et des
30 sucres réducteurs,

- les persulfate de métal alcalin en association avec un acide arylphosphinique, tel que l'acide benzène phosphonique et autres similaires, et des sucres réducteurs.

La quantité d'initiateur à utiliser est déterminée de manière à ce que la quantité de radicaux générés soit d'au plus 20 % en mole par rapport à la quantité de composé (II),
35 de préférence d'au plus 5 % en mole.

monomères zwitterioniques comme par exemple l'acrylate de sulfopropyl (diméthyl)aminopropyle.

Pour la préparation des copolymères de formule (I) pour lesquels $Y = H$ et $Y' = NH_2$, on utilise de préférence à titre de monomères éthyléniquement insaturés les amides de la vinylamine, par exemple le vinylformamide ou le vinylacétamide. Puis le copolymère obtenu est hydrolysé à pH acide ou basique.

Pour la préparation des copolymères de formule (I) pour lesquels $Y = H$ et $Y' = OH$, on utilise de préférence à titre de monomères éthyléniquement insaturés les esters vinyliques d'acide carboxylique, comme par exemple l'acétate de vinyle. Puis le copolymère obtenu est hydrolysé à pH acide ou basique.

Les types et quantités de monomères copolymérisables mis en oeuvre selon la présente invention varient en fonction de l'application finale particulière à laquelle est destiné le polymère à blocs. Ces variations sont bien connues et peuvent être facilement déterminées par l'homme du métier.

Pour que le polymère de formule générale (I) soit un polymère à blocs, le composé "précurseur" de formule générale (II) doit être un polymère.

Donc n est supérieur ou égal à 1, de préférence supérieur ou égal à 6. Les unités monomères de ce polymère peuvent être identiques ou différentes.

Selon la variante préférée de l'invention, dans la formule (II) des composés précurseurs, Z^1 est un atome de soufre et Z^2 est un atome d'oxygène : ces composés sont donc fonctionnalisés en bout de chaîne par des xanthates d'alkyles.

De préférence, dans la formule (II) des composés précurseurs, R^1 représente :

- un groupe de formule $CR^1R^2R^3$, dans laquelle :

R^1 , R^2 et R^3 représentent des groupes (i), (ii) ou (iii) tels que définis ci-dessus, ou

$R^1 = R^2 = H$ et R^3 est un groupe aryle, alcène ou alcyne,

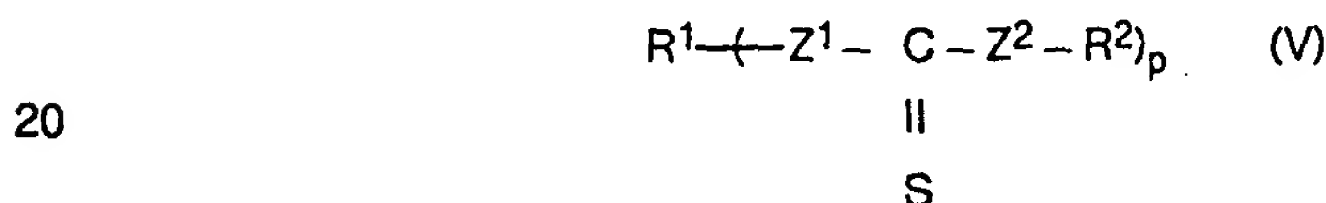
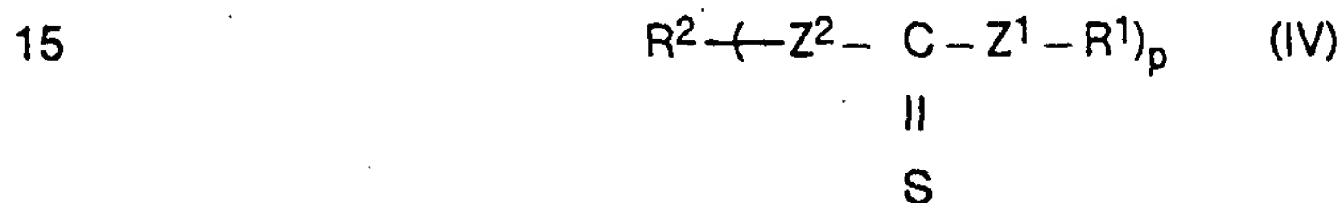
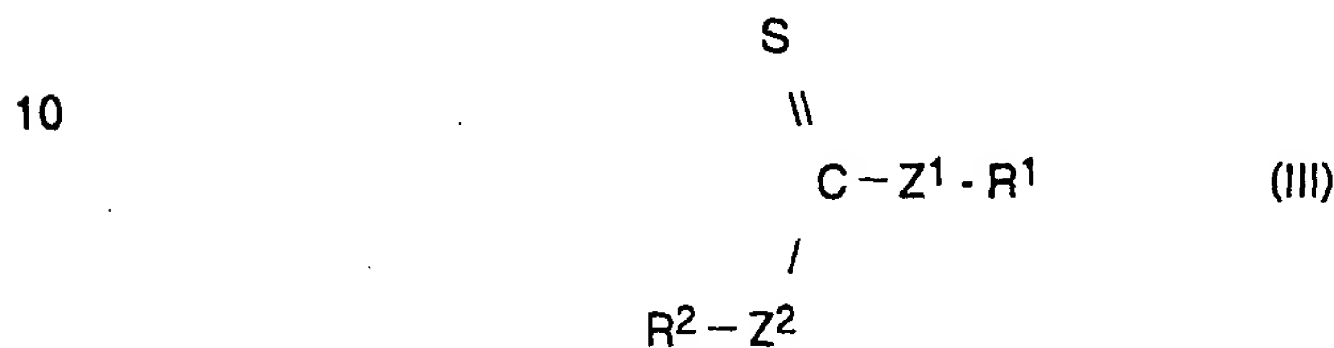
- ou un groupe $-COR^4$ dans lequel R^4 représente un groupe (i), (ii) ou (iii) tel que définis ci-dessus.

De même, dans la formule (II) des composés précurseurs, R^2 représente de préférence un groupe de formule : $-CH_2R^5$, dans laquelle R^5 représente H ou un groupe (i), (ii) ou (iii) à l'exception des groupes aryle, alcyne et alcène.

Les résultats les plus intéressants ont été obtenus pour les composés de formule (II) lorsque Z^1 est un atome de soufre, Z^2 est un atome d'oxygène, R^2 est le groupe éthyl ou phényl, et R^1 est un groupe choisi parmi :

- $Z^1 = S$, $Z^2 = O$, $R^1 = CHCH_3(CO_2Et)$ et $R^2 = Et$, ou
- $Z^1 = S$, $Z^2 = O$, $R^1 = CH(CO_2Et)_2$ et $R^2 = Et$.

5 Ce polymère précurseur (II) peut être issu de la polymérisation radicalaire d'un monomère éthyléniquement insaturé de formule : $CXX' (= CV - CV')_b = CH_2$ par mise en contact dudit monomère avec un initiateur de polymérisation radicalaire et un composé de formule générale (III), (IV) ou (V) :



p étant compris entre 2 et 10, de préférence entre 2 et 5.

Lors de cette synthèse, les initiateurs de polymérisation radicalaire et les monomères éthyléniquement insaturés sont du type de ceux précédemment cités.

25 Quant aux composés de formules générales (III), (IV) ou (V), les symboles R^2 , Z^2 , R^1 et Z^1 ont la même signification que précédemment. Les préférences quant à ses symboles sont les mêmes que précédemment.

Ainsi, les composés de formule générale (III) préférés sont le α -(O-éthylxanthyl)propionate d'éthyle ($Z^1 = S$, $Z^2 = O$, $R^1 = CHCH_3(CO_2Et)$, $R^2 = Et$) et le [1-
30 (O-éthylxanthyl)malonate ($Z^1 = S$, $Z^2 = O$, $R^1 = CH(CO_2Et)_2$, $R^2 = Et$).

Parmi les composés de formule (IV), on préfère ceux pour lesquels R^2 est le groupe $-(CH_2)_q-$ ou un groupe polyéther $-(CHR - CH_2 - O)_q - CHR - CH_2 -$, avec q compris entre 2 et 10.

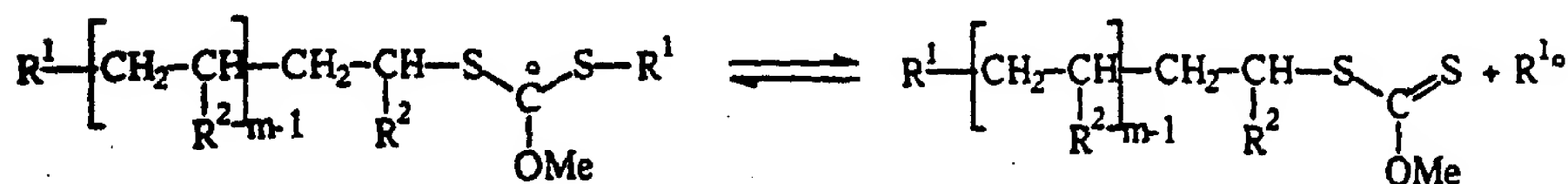
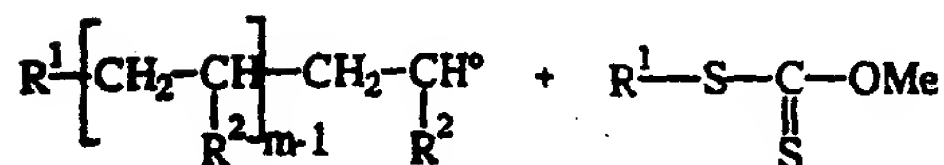
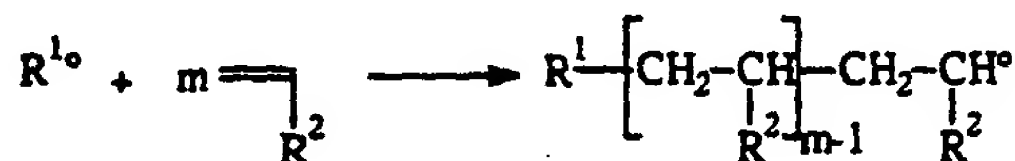
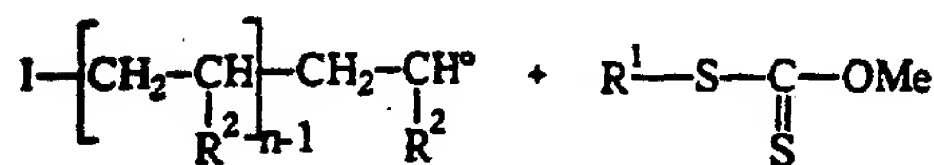
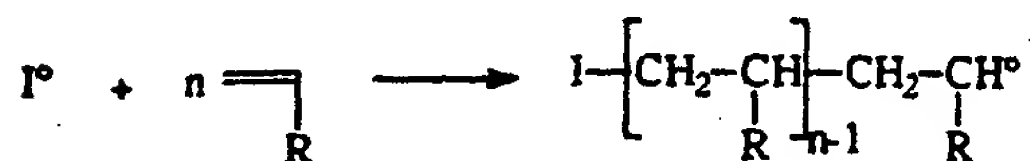
35 Parmi les composés de formule (V), on préfère ceux pour lesquels R^1 est le groupe $-CH_2-$ phényl $-CH_2-$ ou le groupe $-CHCH_3CO_2CH_2CH_2CO_2CHCH_3-$.

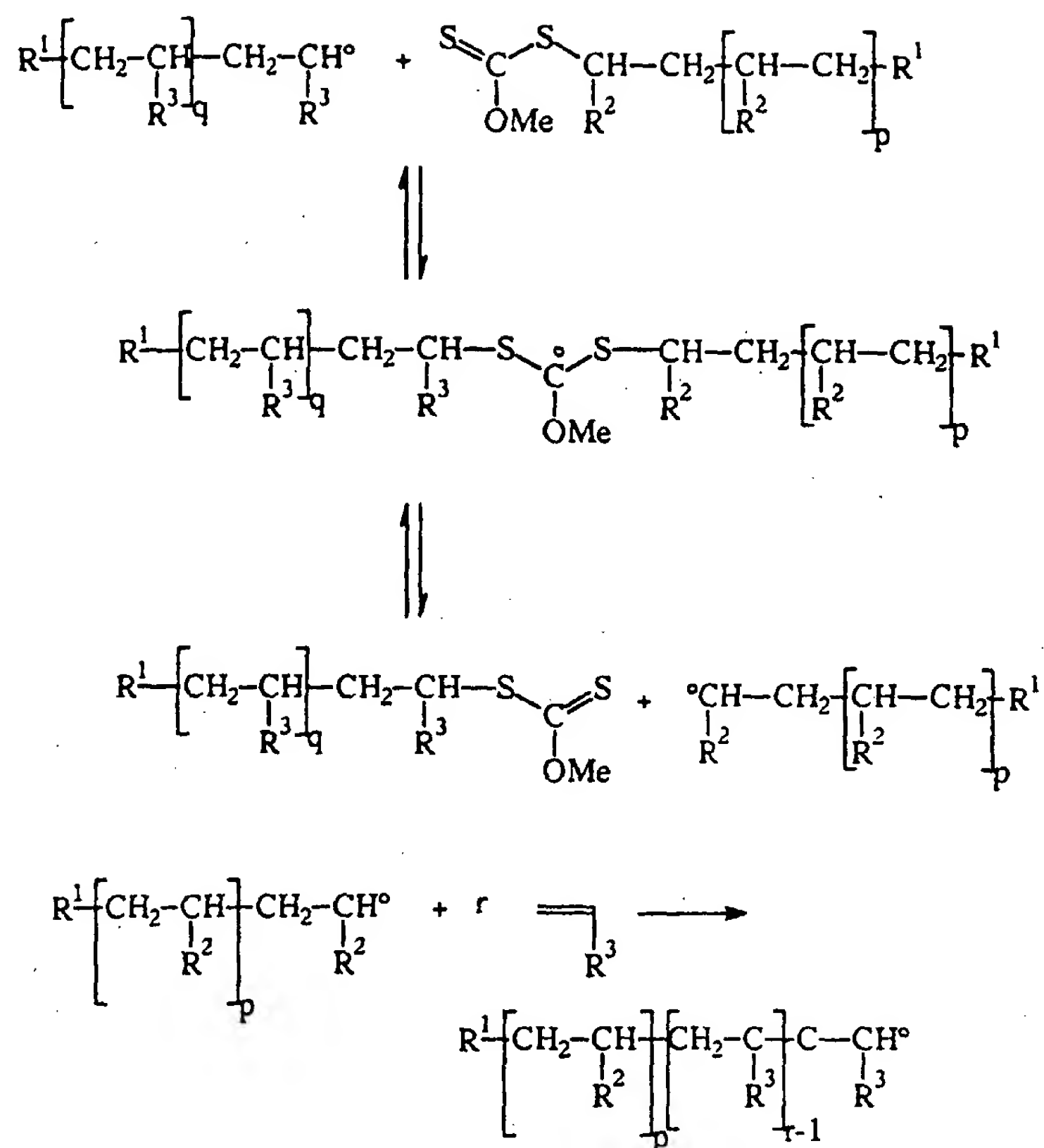
Les composés de formules (III), (IV) et (V) sont facilement accessibles. Ceux pour lesquels Z^1 est un atome de soufre et Z^2 est un atome d'oxygène, dits xanthates

De même, pour la préparation des précurseurs de formule (II) pour lesquels $X = H$ et $X' = OH$, on utilise de préférence à titre de monomères éthyléniquement insaturés les esters vinyliques d'acide carboxylique, comme par exemple l'acétate de vinyle. Puis le polymère obtenu est hydrolysé à pH acide ou basique.

- 5 Sans pour autant exclure tout autre schéma réactionnel, le mécanisme d'action supposé de la polymérisation est illustré ci-dessous dans le cas d'un composé précurseur de formule (II) de type xanthate.

1. Initiation de la polymérisation :





Selon ce principe, l'invention concerne donc également un procédé de préparation de polymères multiblocs, dans lequel on répète au moins une fois la mise en oeuvre du

5 procédé précédemment décrit en utilisant :

- des monomères différents de la mise en oeuvre précédente, et
- à la place du composé précurseur de formule (II) le polymère à blocs issu de la mise en oeuvre précédente.

Si on répète la mise en oeuvre une fois, on obtiendra un polymère tribloc, si on le

10 répète une deuxième fois, on obtiendra un polymère "quadribloc", et ainsi de suite. De cette manière, à chaque nouvelle mise en oeuvre, le produit obtenu est un polymère à blocs présentant un bloc polymère supplémentaire.

Donc, pour la préparation de polymères multiblocs, le procédé consiste à répéter plusieurs fois la mise en oeuvre du procédé précédent sur le polymère à blocs issu de

15 chaque mise en oeuvre précédente avec des monomères différents.

Selon ce procédé de préparation de polymères multiblocs, lorsque l'on souhaite obtenir des polymères à blocs homogènes et non à gradient de composition, et si toutes

Ces polymères présentent, en général, un indice de polydispersité d'au plus 2, de préférence d'au plus 1,5.

Ces résultats sont notamment obtenus pour les polymères à blocs de formule (I) fonctionnalisés en bout de chaîne par le groupe xanthate d'alkyle.

5 Ces polymères correspondent aux polymères de formule générale (I) pour lesquels Z^1 est un atome de soufre et Z^2 est un atome d'oxygène.

Les polymères à blocs préférés sont ceux présentant au moins deux blocs polymères choisis parmi les associations suivantes :

- polystyrène/polyacrylate de méthyle
- 10 - polystyrène/polyacrylate d'éthyle,
- polystyrène/polyacrylate de tertiobutyle,
- polyacrylate d'éthyle/polyacétate de vinyle,
- polyacrylate de butyle/polyacétate de vinyle
- polyacrylate d'éthyle/polyacrylate de tertiobutyle,
- 15 - polyacrylate de tertiobutyle/polyacétate de vinyle,
- polyacrylate d'éthyle/polyacrylate de butyle,
- polyacrylate de butyle/alcool polyvinylique,
- polyacide acrylique/alcool polyvinylique.

20 Selon un mode préféré, les polymères présentent au moins deux blocs polymères choisis parmi les associations précédentes et sont de formule générale (I), dans laquelle :

- $Z^1 = S$, $Z^2 = O$, $R^1 = CHCH_3(CO_2Et)$ et $R^2 = Et$, ou
- $Z^1 = S$, $Z^2 = O$, $R^1 = CH(CO_2Et)_2$ et $R^2 = Et$.

25 Enfin, le procédé de synthèse des polymères précurseurs de formule générale (II) permet également de synthétiser des polymères présentant un faible indice de polydispersité. Ces polymères précurseurs présentent, en général, un indice de polydispersité d'au plus 2, de préférence d'au plus 1,5, notamment lorsque ces polymères sont fonctionnalisés xanthate d'alkyle (Z^1 est un atome de soufre et Z^2 est un

30 atome d'oxygène).

De préférence, n est supérieur ou égal à 6.

Les composés (II) particulièrement préférés sont les homopolymères de styrène ($Y' = H$, $Y = C_6H_5$, $b = 0$), d'acrylate de méthyle ($Y' = H$, $Y = COOMe$, $b = 0$), d'acrylate d'éthyle ($Y' = H$, $Y = COOEt$, $b = 0$), d'acrylate de butyle ($Y' = H$, $Y = COOBu$, $b = 0$),

35 d'acrylate de tertiobutyle ($Y' = H$, $Y = COOtBu$, $b = 0$), d'acétate de vinyle ($Y' = H$, $Y = OCOMe$, $b = 0$), d'acide acrylique ($Y' = H$, $Y = COOH$, $b = 0$), et pour lesquels :

- $Z^1 = S$, $Z^2 = O$, $R^1 = CHCH_3(CO_2Et)$ et $R^2 = Et$, ou
- $Z^1 = S$, $Z^2 = O$, $R^1 = CH(CO_2Et)_2$ et $R^2 = Et$.

Dans un ballon, on introduit environ 1 litre d'éthanol et 80 ml de *a, a'*-dichloro-*p*-xylène. Le ballon est plongé dans un bain de glace. L'homogénéisation se fait sous agitation et balayage d'azote. Lorsque la température du milieu réactionnel est stabilisée, on ajoute 184 g d'O-éthylxanthate de potassium. L'agitation et le balayage d'azote sont maintenus pendant environ 4 heures au cours desquelles le milieu devient blanchâtre en raison de la formation de KCl.

Lorsque la réaction est terminée, environ 1 litre d'eau est additionné dans le réacteur. Le milieu devient limpide et jaune. Le produit désiré est extrait de la phase eau-alcool par un mélange dichlorométhane/éther/pentane (1/1/2) et récupéré par évaporation sous vide.

Le spectre par RMN ^{13}C donne les pics suivants : 135,27 ; 129,42 ; 70,23 ; 40,12 ; 13,89.

15

Exemple 1.4 : Synthèse du précurseur *a*-(O-éthylxanthyl)-*a*-phtalimido acétophenone

Dans un ballon, on introduit 74 ml d'acétone et 12,7 g de *a*-bromo-*a*-phtalimido acétophénone. Le mélange est homogénéisé sous agitation et balayage d'azote. On ajoute 6,5 g de sel O-éthylxanthate de potassium. La réaction dure 5 min, puis le milieu réactionnel est dilué par de l'eau distillée.

Le solide précipité est filtré, séché et purifié par recristallisation dans l'éthanol.

Le spectre par RMN ^{13}C donne les pics suivants : 210,0 ; 189,2 ; 166,2 ; 134,4 ; 133,8 ; 133,6 ; 131,5 ; 128,7 ; 128,4 ; 123,7 ; 71,6 ; 61,8 ; 13,6.

25

Exemple 1.5 : Synthèse du précurseur *a*-(O-éthylxanthyl)-*a*-phénylthiopropionate d'éthyle

30

Dans un ballon, on introduit 11 ml d'acétone et 2,36 g de sel O-éthylxanthate de potassium. Le mélange est homogénéisé sous agitation et balayage d'azote puis, on ajoute au goutte à goutte une solution de *a*-chloro-*a*-phénylthiopropionate d'éthyle (1,56 g) dans l'acétone (4 ml). Le mélange est agité pendant 30 min. Le solvant est évaporé. Le résidu dilué à l'éther, puis lavé à l'eau.

35

La phase organique est séparée et séchée sur du sulfate de sodium. Le produit est récupéré après concentration sous vide et purification par chromatographie sur silice.

On introduit dans un ballon 1 équivalent d'alcool phényléthylique (16,78 ml) en solution dans 150 ml de THF, puis on ajoute 1 équivalent de NaH (5,68 g) à 0°C.

Après deux heures d'agitation, 1 équivalent de CS₂ (8,48 ml) est ajouté.

Après agitation toute la nuit à température ambiante, la solution est filtrée. Le sel
5 est lavé avec du pentane puis séché. Il est isolé d'une manière quantitative sous la forme d'une poudre jaune dont 1,09 g est dissous dans 5 ml d'acétone. La solution est refroidie à 0°C.

1 équivalent (0,99 g) de α -chlorophényléthanoate d'éthyle est ajouté. La solution est agitée pendant trois heures à température ambiante.

10 Elle est ensuite extraite par de l'éther, séchée sur sulfate de magnésium et concentrée sous vide.

1,62 g de α -(O-phényléthylxanthyl)- α -phényléthanoate d'éthyle est récupéré. Le rendement global de réaction est de 90 %.

15 **Exemple 1.9 : Synthèse du précurseur (O-ethylxanthyl)-isobutyronitrile**

On dissout 10 ml de bis(O-ethyl)xanthate (2,42 g) dans 36 ml d'hexane dans un ballon de 100 ml muni d'un réfrigérant et sous atmosphère inerte d'argon.

La solution est chauffée pendant 15 min puis 1 équivalent d'azo-bis-isobutyronitrile
20 (AIBN) (1,64 g) est additionné. 0,5 équivalent d'AIBN (0,82 g) est ajouté après deux heures et demie.

La solution est séchée sous vide. Le produit est purifié par chromatographie et isolé. Le rendement est de 77 %.

25 **Exemple 1.10 : Synthèse du précurseur O-néopentylxanthylmalonate d'éthyle**

Dans un ballon, on introduit 1 équivalent d'alcool néopentylique (2,15 ml) en solution dans 30 ml de THF. Puis, on ajoute 1 équivalent de NaH (0,81 g) à 0°C.

Après deux heures d'agitation, on ajoute 1 équivalent de CS₂ (1,21 ml).

30 Après agitation toute la nuit à température ambiante, la solution est filtrée. Le sel est lavé avec du pentane, puis séché. Il est isolé d'une manière quantitative sous la forme d'une poudre jaune dont 1,86 g est mis en solution dans 10 ml d'acétone. La solution est refroidie à 0°C.

On ajoute 1 équivalent d'éthylchloromalonate (1,61 ml) dans 5 ml d'acétone. La
35 solution est agitée pendant 4 heures à température ambiante. Elle est ensuite hydrolysée et extraite à l'éther. Puis, elle est séchée sur du sulfate de magnésium et concentrée sous vide.

- 0,02 mmol après quatre heures,
- 0,01 mmol après six heures,
- 0,01 mmol après huit heures.

- 5 Le polymère est récupéré par précipitation dans le méthanol et analysé par G.P.C. en milieu THF et en équivalents polystyrène (voir tableau 9).

Exemple 2.2 : Homopolymère de styrène

- 10 Dans un ballon de 10 ml, on introduit 1 mmol de [1-(O-éthylxanthyl)éthyl]benzène (0,226 g) et 40 mmol de styrène (4,16 g). La température est portée à 90°C et on ajoute 0,02 mmol de peroxyde de lauroyle (8,52 mg).

La polymérisation dure 12 heures au cours desquelles on réalise plusieurs ajouts d'amorceur :

- 15 - 0,01 mmol après deux heures,
 - 0,01 mmol après quatre heures,
 - 0,01 mmol après six heures,
 - 0,01 mmol après huit heures,
 - 0,01 mmol après dix heures.

20

Le polymère est récupéré par précipitation dans le méthanol et analysé par G.P.C. en milieu THF et en équivalents polystyrène (voir tableau 9).

Exemple 2.3 : Homopolymère de styrène

25

Dans un ballon de 10 ml, on introduit 1 mmol de a, a'-di(O-éthylxanthyl)-p-xylène (0,346 g) et 40 mmol de styrène (4,16 g). La température est portée à 90°C et on ajoute 0,02 mmol de peroxyde de lauroyle (8,52 mg) .

- 30 La polymérisation dure 15 heures au cours desquelles plusieurs ajouts d'amorceur sont réalisés :

- 0,01 mmol après deux heures,
 - 0,01 mmol après quatre heures,
 - 0,01 mmol après six heures,
 - 0,01 mmol après huit heures,
35 - 0,01 mmol après douze heures,
 - 0,01 mmol après quatorze heures.

Exemple 2.6 : Homopolymère d'acrylate de méthyle

Dans un ballon de 10 ml, on introduit 1 mmol de α -(O-éthylxanthyl)propionate d'éthyle (0,222 g), 40 mmol d'acrylate de méthyle (AMe) (3,44 g) et 3,5 ml de toluène. La température est portée à 100°C et on ajoute 0,035 mmol de peroxyde de lauroyle (14,9 mg). La polymérisation dure 15 heures au cours desquelles on réalise plusieurs ajouts d'amorceur :

- 0,02 mmol après deux heures,
- 0,02 mmol après six heures,
- 0,02 mmol après dix heures.

Le polymère est récupéré par évaporation, sous vide poussé, du solvant et des traces de monomères résiduels et analysé par G.P.C. en milieu THF et en équivalents polystyrène (voir tableau 9).

Exemple 2.7 : Homopolymère d'acrylate de méthyle

Dans un ballon de 10 ml, on introduit 1 mmol de α -(O-éthylxanthyl)propionate d'éthyle (0,222 g) et 40 mmol d'acrylate de méthyle (3,44 g). La température est portée à 80°C et on ajoute 0,03 mmol de peroxyde de lauroyle (12,8 mg).

La polymérisation dure 45 min.

Le polymère est récupéré par évaporation, sous vide poussé, du solvant et des traces de monomères résiduels. Il est analysé par G.P.C. en milieu THF et en équivalents polystyrène (voir tableau 9).

Exemple 2.8 : Homopolymère d'acrylate de méthyle

Dans un ballon de 10 ml, on introduit 1 mmol de α -(O-éthylxanthyl)propionate d'éthyle (0,222 g) et 80 mmol d'acrylate de méthyle (6,88 g). La température est portée à 80°C et 0,02 mmol de peroxyde de lauroyle (8,52 mg) sont ajoutées. La polymérisation dure 45 min.

Le polymère est récupéré par évaporation, sous vide poussé, des traces de monomères résiduels. Il est analysé par G.P.C. en milieu THF et en équivalents polystyrène (voir tableau 9).

Le polymère est récupéré par évaporation, sous vide poussé, des traces de monomères résiduels. Il est analysé par G.P.C. en milieu THF et en équivalents polystyrène (voir tableau 9).

5 Exemple 2.13 : homopolymère d'acétate de vinyle

Dans un ballon de 10 ml, on introduit 1 mmol de α -(O-éthylxanthyl)propionate d'éthyle (0,222 g) et 40 mmol d'acétate de vinyle (AVM) (3,44 g). La température est portée à 80°C et on ajoute 0,02 mmol de peroxyde de lauroyle (8,52 mg).

10 La polymérisation dure 8 heures au cours desquelles on réalise plusieurs ajouts d'amorceur :

- 0,01 mmol après deux heures,
- 0,01 mmol après quatre heures,
- 0,01 mmol après six heures.

15

Le polymère est récupéré par évaporation, sous vide poussé, des traces de monomères résiduels et analysé par G.P.C. en milieu THF et en équivalents polystyrène (voir tableau 9).

20 Exemple 2.14 : Homopolymère d'acétate de vinyle

Dans un ballon de 10 ml, on introduit 1 mmol de α -(O-éthylxanthyl)propionate d'éthyle (0,222 g) et 40 mmol d'acétate de vinyle (3,44 g). La température est portée à 80°C et on ajoute 0,02 mmol de peroxyde de lauroyle (8,52 mg).

25 La polymérisation dure 4 heures.

Le polymère est récupéré par évaporation, sous vide poussé, des traces de monomères résiduels. Il est analysé par G.P.C. en milieu THF et en équivalents polystyrène (voir tableau 9).

30 Exemple 2.15 : Homopolymère de styrène

Dans un ballon de 10 ml, on introduit 1 mmol (3,8 g) du polymère issu de l'exemple 2.1, fonctionnalisé en bout de chaîne par le groupement O-éthylxanthyle, et 40 mmol de styrène (4,16 g). La température est portée à 90°C et on ajoute 0,02 mmol
35 de peroxyde de lauroyle (8,52 mg).

La polymérisation dure 10 heures au cours desquelles on réalise plusieurs ajouts d'amorceur :

- 0,01 mmol après deux heures,

Le polymère est récupéré par précipitation dans le méthanol.

Il est analysé par G.P.C. en milieu THF et en équivalents polystyrène (voir tableau 9).

5 **Exemple 2.18 : Homopolymère d'acrylate de méthyle**

10 Dans un ballon de 10 ml contenant 4 ml de toluène, on introduit 1 mmol de O-éthylxanthylmalonate (0,28 g) et 40 mmol d'acrylate de méthyle (3,44 g). La température est portée à 80°C et on ajoute 0,03 mmol de peroxyde de lauroyle (12,8 mg).

La polymérisation dure 26 heures au cours desquelles 0,02 mmol de peroxyde de lauroyle sont ajoutées toutes les deux heures.

15 Le polymère est récupéré par évaporation sous vide poussé du toluène et des traces de monomère résiduel.

Il est analysé par G.P.C. en milieu THF et en équivalents polystyrène (voir tableau 9).

20 **Exemple 2.19 : Homopolymère de styrène**

Dans un ballon de 10 ml, on introduit 1 mmol de α -(O-phényléthyl)- α -phénylthiopropionate d'éthyle (0,406 g) et 40 mmol de styrène (4,16 g). La température est portée à 95°C et on ajoute 0,03 mmol de peroxyde de lauroyle (12,8 mg).

25 La polymérisation dure 16 heures au cours desquelles 0,02 mmol de peroxyde de lauroyle sont ajoutées toutes les deux heures.

Le polymère est récupéré par précipitation dans le méthanol.

Il est analysé par G.P.C. en milieu THF et en équivalents polystyrène (voir tableau 9).

30

Exemple 2.20 : Homopolymère d'acrylate de méthyle

35 Dans un ballon de 10 ml, on introduit 1 mmol de α -(O-phényléthylxanthyl)- α -phényléthanoate d'éthyle (0,36 g) et 40 mmol d'acrylate de méthyle (3,44 g). La température est portée à 80°C et on ajoute 0,03 mmol de peroxyde de lauroyle (12,8 mg).

La polymérisation dure 11 heures au cours desquelles 0,02 mmol de peroxyde de lauroyle sont ajoutées toutes les deux heures.

La polymérisation dure 2h30 au cours desquelles 0,02 mmol de peroxyde de lauroyle sont ajoutées après 2 heures.

5 Le polymère est récupéré par évaporation, sous vide poussé, des traces de monomères résiduels.

Il est analysé par G.P.C. en milieu THF et en équivalents polystyrène (voir tableau 9).

Exemple 2.24 : Homopolymère d'acétate de vinyle

10

Dans un ballon de 10 ml, on introduit 1 mmol O-isobornylmalonate d'éthyle (0,388 g) et 77 mmol d'acétate de vinyle (6,62 g). La température est portée à 70°C et on ajoute 0,01 mmol d'AIBN (azo-bis-isobutyronitrile) (1,64 mg). La polymérisation dure 24 heures au cours desquelles plusieurs ajouts d'AIBN sont réalisés :

- 15 - 1,4 mg après deux heures,
- 2,2 mg après quatre heures.

Le polymère est récupéré par évaporation sous vide poussé des traces de monomères résiduels.

20 Il est analysé par G.P.C. en milieu THF et en équivalents polystyrène (voir tableau 9).

Exemple 2.25 : Homopolymères d'acide acrylique

25 On dissout 25 g d'acide acrylique dans 85 g d'eau, puis on neutralise la solution ainsi obtenue jusqu'à pH compris entre 6 et 7 : cette solution est la solution 1.

On dissout 0,35g de dihydrochlorure de 2,2'-azobis(2-méthylpropionamide) dans 150 g d'eau : cette solution est la solution 2.

30 Dans trois ballons contenant chacun une quantité différente de (O-isopropylxanthyl)valeronitrile on introduit 11 g de la solution 1 et 1,5 g de la solution 2. Les compositions des différents ballons sont résumées dans le tableau A.

La température est portée à 70°C et la polymérisation est conduite pendant 24 heures.

35 Le polymère est récupéré par évaporation sous vide poussé de l'eau et des traces de monomère résiduel.

Il est analysé par G.P.C. en milieu aqueux et en équivalents POE, les résultats sont rassemblés dans le tableau 1.

Tableau 2

masse AA (g)	masse AIBN (mg)	masse précurseur (g)	Mn	Ip
1,53	3,47	0,35	345	1,12
3,39	1,81	0,2	770	1,10
3,85	1,15	0,13	1060	1,25
4,08	0,92	0,10	1290	1,30

Exemple 2.28 : Homopolymères d'acide acrylique

Plusieurs homopolymères d'acide acrylique sont préparés en solution de la façon suivante.

Dans un ballon, on dissout la totalité de l'acide acrylique (AA), l'AIBN et le précurseur α -(O-éthylxanthyl)propionate d'éthyle dans de l'acétone. Les quantités respectives de chaque ingrédient sont résumés dans le tableau 3.

La température est portée à 60°C.

La polymérisation dure 3 heures.

Les traces de monomère résiduel et le solvant sont éliminés par évaporation.

Les résultats, obtenus après analyse G.P.C. en milieu THF et en équivalents polystyrène, sont résumés dans le tableau 3.

Tableau 3

masse AA (g)	masse AIBN (mg)	masse de précurseur (g)	volume de solvant (ml)	Mn	Ip
5,07	2,93	0,3	8	550	1,10
3,88	1,12	0,12	5	1170	1,19
4,37	0,63	0,07	5	1760	1,29
4,56	0,44	0,05	5	1920	1,27

La température est ensuite augmentée jusqu'à 85°C et on ajoute en une fois 0,4 g de persulfate d'ammonium en solution dans 16,13 g d'eau.

Une alimentation continue de styrène (180 g) est alors mise en place sur quatre heures.

5 La température est maintenue à 85°C pendant 2 heures supplémentaires.

Les résultats, obtenus après analyse G.P.C. en milieu THF et en équivalents polystyrène, sont résumés dans le tableau 5.

Tableau 5

10

Masse de précurseur (g)	Taux de conversion (%)	Mn	Ip
2	88	15 400	1,9
1	90	29 500	1,9

Exemple 2.32 : Homopolymère de styrène obtenu en émulsion

On introduit dans un réacteur de 1,5 l équipé d'une ancre en teflon :

- 15
- 475 g d'eau,
 - 0,2 g d'hydrogénocarbonate de sodium et
 - 10 g de laurylsulfate de sodium .

La température est portée à 70°C et on additionne en une fois :

- 20
- 20 g de styrène, et
 - 2 g de α -(O-éthylxanthyl)propionate d'éthyle.

La température est ensuite augmentée jusqu'à 85°C et on ajoute en une fois 0,4 g de persulfate d'ammonium en solution dans 16,13 g d'eau.

On introduit dans le réacteur en continu et en parallèle :

- 25
- 180 g de styrène sur 8 heures,
 - 0,4 g de persulfate d'ammonium dans 50,4 g d'eau sur 10 heures.

Des échantillons sont prélevés régulièrement et analysés en G.P.C. en milieu THF et en équivalents polystyrène. Les résultats obtenus sont résumés dans le tableau 6.

Tableau 7

Temps (min)	Taux de conversion (%)	Mn	Ip
12	0	1 900	3,4
21	17	4 200	2,5
30	32,3	4 300	2,5
42	43,5	4 800	2,4
53	46,6	4 800	2,5
66	71,4	6 700	1,9
124	80,4	7 100	1,9

- 5 On observe une augmentation linéaire des masses moléculaires avec la conversion, ce qui prouve le caractère contrôlé de la polymérisation radicalaire.

Exemple 2.34 : Homopolymère d'acétate de vinyle

- 10 On prépare une solution contenant :
- 7,35g d'acétate de vinyle,
 - 0,229 g de α -(O-éthylxanthyl)propionate d'éthyle, et
 - 0,018 g d'AIBN.
- On introduit 1 g de cette solution dans 4 tubes qui serviront à établir la cinétique
- 15 de polymérisation.
- Les tubes sont ensuite portés à 70°C et arrêtés à des temps différents. Pour chaque tube, le polymère est récupéré par évaporation des traces de monomère résiduel et analysé en G.P.C. en milieu THF et en équivalents polystyrène.
- Les résultats obtenus sont rassemblés dans le tableau 8.

Tableau 9

Exemples	Monomère	Mn	Ip	Taux de conversion
Ex. 2.1	styrène	3800	2	
Ex. 2.2	styrène	5200	2,1	
Ex. 2.3	styrène	7900	2,5	
Ex. 2.4	styrène	3200	1,8	
Ex. 2.5	styrène	3300	1,9	
Ex. 2.6	AMe	3500	1,8	
Ex. 2.7	AMe	3750	1,7	
Ex. 2.8	AMe	7300	1,7	
Ex. 2.9	AMe	3000	1,4	
Ex. 2.10	AEt	3700	1,6	
Ex. 2.11	AMe	3500	1,35	
Ex. 2.12	A2EH	6900	1,5	
Ex. 2.13	AVM	3200	1,35	
Ex. 2.14	AVM	2100	1,18	
Ex. 2.15	styrène	6200	2	
Ex. 2.16	styrène	3800	1,6	
Ex. 2.17	styrène	4300	1,9	78
Ex. 2.18	AMe	3900	1,5	95
Ex. 2.19	styrène	3400	1,8	77
Ex. 2.20	AMe	3100	1,6	60
Ex. 2.21	AMe	3600	1,4	75
Ex. 2.22	AMe	5100	1,4	90
Ex. 2.23	AMe	4000	1,7	88
Ex. 2.24	AVM ?	2500	1,8	29
Ex. 2.26	AA	6600	2,3	97
Ex. 2.29	AEt	29 400	1,9	93

5

Exemple 2.35 : homopolymère d'acétate de vinyle

On introduit dans un ballon de 10 ml :

- 0,899g d'acétate de vinyle (soit environ 10 équivalents),

de méthyle résiduel. Cette synthèse conduit à un précurseur utilisable pour la préparation d'un copolymère à blocs.

5 On introduit ensuite 20 mmol de styrène (2,08 g) dans le réacteur. La température est portée à 110°C et on ajoute 0,02 mmol de peroxyde de lauroyle (8,52 mg). Cette deuxième étape dure 6 heures au cours desquelles on réalise plusieurs ajouts d'amorceur :

- 0,01 mmol après deux heures,
- 0,01 mmol après quatre heures.

10

Le copolymère obtenu est récupéré par précipitation dans le méthanol et analysé en G.P.C. double détection : réfractométrie et spectrométrie UV. Le solvant de G.P.C. est le THF et les masses sont données en équivalents polystyrène. Les résultats sont donnés dans le tableau 12.

15

Exemple 3.2 : Copolymère à blocs p(St-b-AMe)

Dans un ballon de 10 ml, on introduit :

- 1 mmol de a-(O-éthylxanthyl)propionate d'éthyle (0,222 g),
- 20 - 20 mmol de styrène (2,08 g), et
- 1 ml de toluène.

Le milieu réactionnel est porté à 110°C et on introduit 0,025 mmol de peroxyde de lauroyle (10,6 mg) dans le réacteur. Cette première étape dure 9 heures au cours desquelles on réalise plusieurs ajouts d'amorceur :

- 25 - 0,01 mmol après deux heures,
- 0,01 mmol après quatre heures,
- 0,01 mmol après six heures,
- 0,01 mmol après huit heures.

30

Le milieu est ensuite refroidi jusqu'à 80°C et on introduit :

- 20 mmol d'acrylate de méthyle (1,72 g), et
- 0,03 mmol de peroxyde de lauroyle (12,8 mg).

Cette seconde étape dure 7 heures au cours desquelles on réalise plusieurs additions d'amorceur :

- 35 - 0,01 mmol après deux heures,
- 0,01 mmol après quatre heures,
- 0,01 mmol après six heures.

- 0,01 mmol après deux heures,
- 0,01 mmol après quatre heures,
- 0,01 mmol après six heures,
- 0,01 mmol après huit heures.

5

Le milieu réactionnel est ensuite refroidi à 80°C et on introduit :

- 20 mmol d'acrylate de méthyle, et
- 0,02 mmol de peroxyde de lauroyle.

Cette deuxième étape dure 8 heures au cours desquelles on réalise plusieurs

10 ajouts d'amorceur :

- 0,01 mmol après deux heures,
- 0,01 mmol après quatre heures,
- 0,01 mmol après six heures,
- 0,01 mmol après sept heures.

15

La température est de nouveau portée à 90°C et on introduit :

- 20 mmol de styrène (2,08 g), et
- 0,02 mmol de peroxyde de lauroyle.

Cette troisième étape dure 8 heures au cours desquelles on réalise plusieurs

20 ajouts d'amorceur :

- 1 mmol après deux heures,
- 1 mmol après quatre heures,
- 1 mmol après six heures.

25

Le polymère obtenu est récupéré et analysé comme celui de l'exemple 3.1. Les résultats sont donnés dans le tableau 12.

Exemple 3.5 : Copolymère à blocs p(AMe-b-St)

30

Dans un ballon, on introduit :

- 1 mmol de [1-(O-éthylxanthyl)éthyl]benzène (0,226 g), et
- 20 mmol d'acrylate de méthyle (1,72 g).

La température est portée à 80°C et on ajoute 0,02 mmol de peroxyde de lauroyle.

Cette première étape dure 8 heures au cours desquelles sont réalisés plusieurs ajouts

35 d'amorceur :

- 1 mmol après deux heures,
- 1 mmol après quatre heures,
- 1 mmol après six heures.

- 8,5 mg après 4 heures.

Les traces d'acétate de vinyle résiduel sont éliminées par évaporation sous vide poussé. Les résultats sont donnés dans le tableau 12.

5

Exemple 3.7 : Copolymère à blocs p(AEt-b-AtBu)

On introduit dans un ballon :

- 1,881 g d'acrylate d'éthyle,
- 10 - 0,111 g de α -(O-éthylxanthyl)propionate d'éthyle et,
- 9,0 mg de peroxyde de lauroyle. La température est portée à 80°C. La polymérisation dure 6 heures au cours desquelles on réalise plusieurs ajouts de peroxyde de lauroyle :

- 8,6 mg après 2 heures,
- 15 - 8,9 mg après 4 heures.

Après refroidissement, les traces d'acrylate d'éthyle résiduel sont éliminées par évaporation sous vide poussé et une petite fraction du polymère est prélevée pour être analysé en G.P.C. en milieu THF et en équivalents polystyrène:

- 20 - taux de conversion : 98,6%,
- $M_n = 2\ 600$,
- $I_p = 1,9$.

On introduit ensuite dans le ballon :

- 25 - 2,7467 g d'acrylate de tertiobutyle, et
- 8,5 mg de peroxyde de lauroyle.

La température est portée à 80°C. La polymérisation dure 6 heures au cours desquelles on réalise plusieurs ajouts de peroxyde de lauroyle :

- 8,7 mg après 2 heures,
- 30 - 8,5 mg après 4 heures.

Les traces d'acrylate de tertiobutyle résiduel sont éliminées par évaporation sous vide poussé et le copolymère obtenu est analysé par G.P.C. en milieu THF et en équivalents polystyrène. Les résultats sont donnés dans le tableau 12.

35

Exemple 3.8 : Copolymère à blocs p(AtBu-b-AVM)

On introduit dans un ballon :

Après refroidissement, les traces d'acrylate de tertibutyle résiduel sont éliminées par évaporation sous vide poussé et une petite fraction du polymère est prélevée pour être analysé en G.P.C. en milieu THF et en équivalents polystyrène :

- taux de conversion : 98,1 %,
- 5 - $M_n = 2\,500$,
- $I_p = 2,5$.

On introduit dans le ballon :

- 1,896 g d'acrylate d'éthyle, et
- 10 - 8,8 mg de peroxyde de lauroyle.

La température est portée à 80°C. La polymérisation dure 6 heures au cours desquelles on réalise plusieurs ajouts de peroxyde de lauroyle :

- 8,7 mg après 2 heures,
- 15 - 8,5 mg après 4 heures.

Les traces d'acrylate d'éthyle résiduel sont éliminées par évaporation sous vide poussé et le copolymère obtenu est analysé par G.P.C. en milieu THF et en équivalents polystyrène. Les résultats sont donnés dans le tableau 12.

20 Exemple 3.10 : Copolymère à blocs p(AEt-b-St)

On introduit dans un ballon :

- 1,881 g d'acrylate d'éthyle,
- 0,111g de α -(O-éthylxanthyl)propionate d'éthyle, et
- 25 - 8,8 mg de peroxyde de lauroyle.

La température est portée à 80°C. La polymérisation dure 6 heures au cours desquelles on réalise plusieurs ajouts de peroxyde de lauroyle :

- 9,0 mg après 2 heures,
- 30 - 8,5 mg après 4 heures.

Après refroidissement, les traces d'acrylate d'éthyle résiduel sont éliminées par évaporation sous vide poussé et une petite fraction du polymère est prélevée pour être analysé en G.P.C. en milieu THF et en équivalents polystyrène :

- taux de conversion : 97,5 %,
- 35 - $M_n = 3\,000$,
- $I_p = 1,8$.

On introduit ensuite dans le ballon :

Les traces de styrène résiduel sont éliminées par évaporation sous vide poussé et le copolymère obtenu est analysé par G.P.C. en milieu THF et en équivalents polystyrène. Les résultats sont donnés dans le tableau 12.

5 **Exemple 3.12 : Copolymère à blocs p(AEt-b-AtBu-b-St)**

On introduit dans un ballon :

- 2,248 g de styrène,
- la totalité du copolymère obtenu à l'exemple 3.7, et
- 10 - 8,3 mg de peroxyde de lauroyle.

La température est portée à 115°C. La polymérisation dure 6 heures au cours desquelles on réalise plusieurs ajouts de peroxyde de lauroyle :

- 9,0 mg après 2 heures,
- 15 - 8,5 mg après 4 heures.

Les traces de styrène résiduel sont éliminées par évaporation sous vide poussé et le copolymère obtenu est analysé par G.P.C. en milieu THF et en équivalents polystyrène. Les résultats sont donnés dans le tableau 12.

20 **Exemple 3.13 : Copolymère à blocs p(St-b-AEt)**

On introduit dans un ballon :

- 2,224 g de styrène,
- 0,111g de a-(O-éthylxanthyl)propionate d'éthyle, et
- 25 - 8,6 mg de peroxyde de lauroyle.

La température est portée à 115°C. La polymérisation dure 6 heures au cours desquelles on réalise plusieurs ajouts de peroxyde de lauroyle :

- 8,7 mg après 2 heures,
- 30 - 8,3 mg après 4 heures.

Après refroidissement, les traces de styrène résiduel sont éliminées par évaporation sous vide poussé et une petite fraction du polymère est prélevée pour être analysé en G.P.C. en milieu THF et en équivalents polystyrène :

- taux de conversion : 98,0 %,
- 35 - $M_n = 3\,500$,
- $I_p = 2,2$.

On introduit ensuite dans le ballon :

Les traces d'acrylate de tertibutyle résiduel sont éliminées par évaporation sous vide poussé et le copolymère obtenu est analysé par G.P.C. en milieu THF et en équivalents polystyrène. Les résultats sont donnés dans le tableau 12.

5

Exemple 3.15 : Copolymère à blocs p(AtBu-b-AEt-b-St)

On introduit dans un ballon :

- 2 ml de toluène,
- 10 - 2,229 g de styrène,
- la totalité du copolymère obtenu à l'exemple 3.9, et
- 9,1 mg de peroxyde de lauroyle.

La température est portée à 120°C. La polymérisation dure 6 heures au cours desquelles on réalise plusieurs ajouts de peroxyde de lauroyle :

- 15 - 8,5 mg après 2 heures,
- 8,5 mg après 4 heures.

Les traces de styrène résiduel sont éliminées par évaporation sous vide poussé et le copolymère obtenu est analysé par G.P.C. en milieu THF et en équivalents polystyrène. Les résultats sont donnés dans le tableau 12.

20

Exemple 3.16 : Copolymères à blocs pABu-b-APV (APV : alcool polyvinylique)

Ces copolymères sont obtenus par hydrolyse de leurs équivalents p(ABu-b-AVM).

25

On prépare une série de copolymères à blocs p(ABu-b-AVM). Tous les copolymères sont obtenus selon le mode opératoire général suivant.

On introduit dans un ballon :

- l'acrylate de butyle (ABu),
- 30 - le a-(O-éthylxanthyl)propionate d'éthyle, et
- environ un tiers de la quantité globale de peroxyde de lauroyle nécessaire à cette première étape.

La température est portée à 80°C. La polymérisation dure 6 heures au cours desquelles sont réalisés deux ajouts d'amorceur après 2 et 4 heures. Chacun des ajouts correspond à environ un tiers de la quantité globale de peroxyde de lauroyle de la première étape.

35

Les traces d'acrylate de butyle résiduel sont éliminées par évaporation et une petite fraction du polymère est prélevée pour être analysée.

Exemple 3.17 : Copolymère à blocs pAA-b-APV

Ce copolymère est obtenu par hydrolyse du copolymère correspondant p(AtBu-b-AVM).

5

On introduit dans un ballon :

- 2,737 g d'acrylate de tertiobutyle,
- 0,111 g de α -(O-éthylxanthyl)propionate d'éthyle, et
- 8,5 mg de peroxyde de lauroyle.

10

La température est portée à 80°C.

La polymérisation dure 6 heures au cours desquelles sont réalisés plusieurs ajouts de peroxyde de lauroyle :

- 9,5 mg après 2 heures,
- 9,8 mg après 4 heures.

15

Après refroidissement, les traces d'acrylate de tertiobutyle résiduel sont éliminées par évaporation sous vide poussé.

Une petite fraction du polymère est prélevée pour être analysé en G.P.C. en milieu THF et en équivalents polystyrène :

20

- taux de conversion : 99,0 %,
- $M_n = 4300$,
- $I_p = 1,7$.

On introduit ensuite dans le ballon :

25

- 1,831 g d'acétate de vinyle, et
- 8,6 mg de peroxyde de lauroyle.

La température est portée à 80°C.

La polymérisation dure 6 heures au cours desquelles sont réalisés plusieurs ajouts de peroxyde de lauroyle :

30

- 9,2 mg après 2 heures,
- 9,2 mg après 4 heures.

Les traces d'acétate de vinyle résiduel sont éliminées par évaporation sous vide poussé et le copolymère obtenu est analysé par G.P.C. en milieu THF et en équivalents polystyrène. Les résultats sont donnés dans le tableau 12.

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Le copolymère obtenu est ensuite hydrolysé de la manière suivante.

- 0,32 g d'AIBN.

La température et l'agitation sont maintenues encore une heure après la fin d'addition du deuxième monomère.

Le copolymère final est récupéré par évaporation du solvant et des traces de monomères résiduel et analysé en G.P.C. en milieu THF et en équivalents polystyrène. Les résultats sont donnés dans le tableau 12.

Exemple 3.19 : Copolymère à blocs p(ABu-b-AEt)

On introduit dans un réacteur muni d'un système d'agitation :

- 45 g d'acétate d'isopropyle,
- 75 g d'acrylate de butyle, et
- 6,9 g de α -(O-éthylxanthyl)propionate d'éthyle.

La température est portée à 80°C et on additionne en une fois 0,15 g d'AIBN en solution dans 5 g d'acétate d'isopropyle.

Vingt minutes plus tard, on met en place une alimentation continue sur 1h30 d'une solution contenant :

- 117 g d'acétate d'isopropyle,
- 175 g d'acrylate de butyle, et
- 0,35 g d'AIBN.

La température et l'agitation sont maintenues 2h10 après la fin d'addition du premier monomère.

Une petite fraction du polymère précurseur est prélevée et analysée en G.P.C. en milieu THF et en équivalents polystyrène :

- $M_n = 5\,200$,
- $I_p = 1,8$.

Une deuxième alimentation continue est alors mise en place sur 1h40. Elle consiste en une solution contenant :

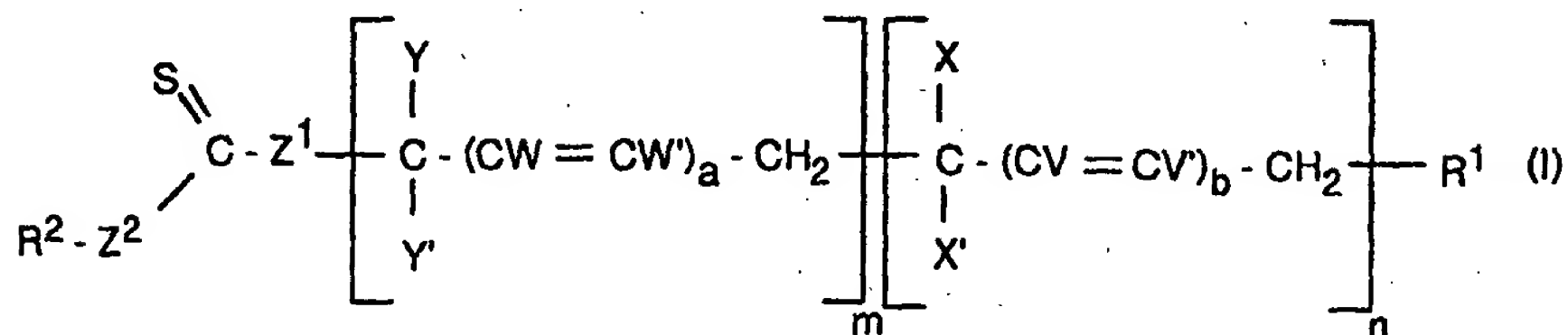
- 168 g d'acétate d'isopropyle,
- 252 g d'acrylate d'éthyle, et
- 0,5 g d'AIBN.

La température et l'agitation sont maintenues encore 20 min après la fin d'addition du deuxième monomère.

Le copolymère final est récupéré par évaporation du solvant et des traces de monomères résiduel et analysé en G.P.C. en milieu THF et en équivalents polystyrène. Les résultats sont donnés dans le tableau 12.

REVENDICATIONS

1. Procédé de préparation de polymères à blocs de formule générale (I) :



dans laquelle :

- Z¹ = S ou P,

- Z² = O, S ou P,

10 - R¹ et R², identiques ou différents, représentent :

. un groupe (i) alkyle, acyle, aryle, alcène ou alcyne éventuellement substitué,
ou

. un cycle (ii) carboné, saturé ou non, éventuellement substitué ou aromatique,
ou

15 . un hétérocycle (iii), saturé ou non, éventuellement substitué,

ces groupes et cycles (i), (ii) et (iii) pouvant être substitués par des groupes
phényles substitués, des groupes aromatiques substitués ou des groupes :
alkoxycarbonyle ou aryloxy carbonyle (-COOR), carboxy (-COOH), acyloxy (-
O₂CR), carbamoyle (-CONR₂), cyano (-CN), alkylcarbonyle, alkylarylcabonyle,
20 arylcarbonyle, arylalkylcarbonyle, phtalimido, maleïmido, succinimido, amidino,
guanidimo, hydroxy (-OH), amino (-NR₂), halogène, allyle, époxy, alkoxy (-OR),
S-alkyle, S-aryle, des groupes présentant un caractère hydrophile ou ionique
tels que les sels alcalins d'acides carboxyliques, les sels alcalins d'acide
sulfonique, les chaînes polyoxyde d'alkylène (POE, POP), les substituants
25 cationiques (sels d'ammonium quaternaires),

R représentant un groupe alkyle ou aryle,

. une chaîne polymère,

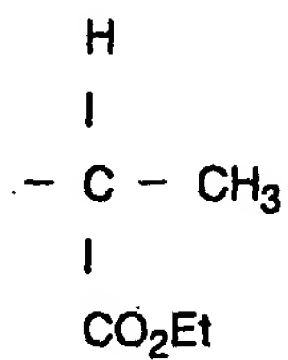
- V, V', W et W', identiques ou différents, représentent : H, un groupe alkyle ou un
halogène,

30 - X, X', Y et Y', identiques ou différents, représentent H, un halogène ou un groupe
R³, OR³, O₂COR³, NHCOH, OH, NH₂, NHR³, N(R³)₂, (R³)₂N⁺O⁻, NHCOR³, CO₂H,
CO₂R³, CN, CONH₂, CONHR³ ou CONR³₂, dans lesquels R³ est choisi parmi les
groupes alkyle, aryle, aralkyle, alkaryle, alcène ou organosilyle, éventuellement

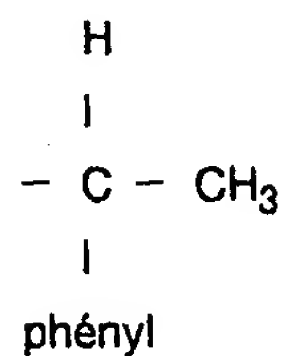
7. Procédé selon la revendication précédente, caractérisé en ce que :

- R¹ est choisi parmi les groupes :

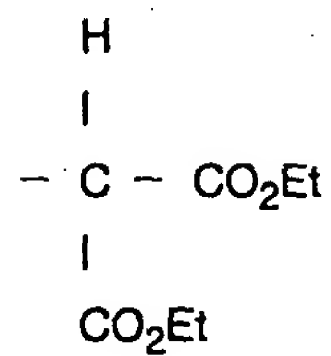
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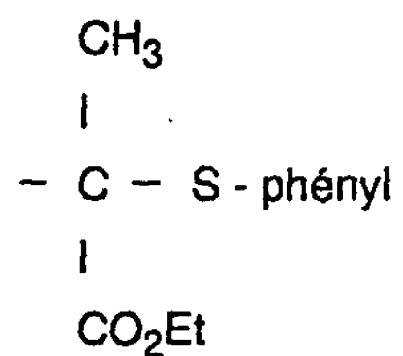
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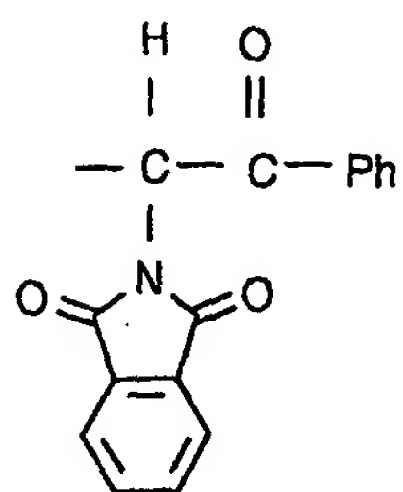
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30 - et R² est un groupe éthyl ou phényl.

11. Procédé de préparation de polymères à blocs, caractérisé en ce qu'on répète au moins une fois la mise en oeuvre du procédé selon l'une des revendications 1 à 10 en utilisant :

- des monomères différents de la mise en oeuvre précédente, et
- 5 - à la place du composé précurseur de formule (II) le polymère à blocs issu de la mise en oeuvre précédente.

12. Polymère à blocs susceptible d'être obtenu par le procédé selon l'une des revendications 1 à 10 ou 11.

10

13. Polymère à blocs selon la revendication précédente, caractérisé en ce qu'il présente un indice de polydispersité d'au plus 2.

14. Polymère à blocs selon la revendication 12 ou 13, caractérisé en ce qu'il présente
15 un indice de polydispersité d'au plus 1,5.

15. Polymère à blocs selon l'une quelconque des revendications 12 à 14, caractérisé en ce qu'il est de formule générale (I) dans laquelle Z^1 est un atome de soufre et Z^2 est un atome d'oxygène.

20

16. Polymère à blocs selon l'une quelconque des revendications 12 à 15, caractérisé en ce qu'ils présentent au moins deux blocs polymères choisis parmi les associations suivantes :

- polystyrène/polyacrylate de méthyle
- 25 - polystyrène/polyacrylate d'éthyle,
- polystyrène/polyacrylate de tertiobutyle,
- polyacrylate d'éthyle/polyacétate de vinyle,
- polyacrylate de butyle/polyacétate de vinyle
- polyacrylate d'éthyle/polyacrylate de tertiobutyle,
- 30 - polyacrylate de tertiobutyle/polyacétate de vinyle,
- polyacrylate d'éthyle/polyacrylate de butyle,
- polyacrylate de butyle/alcool polyvinylique,
- polyacide acrylique/alcool polyvinylique.

35 17. Polymère à blocs selon la revendication 16, caractérisé en ce qu'il est de formule générale (I), dans laquelle :

- $Z^1 = S$, $Z^2 = O$, $R^1 = CHCH_3(CO_2Et)$ et $R^2 = Et$, ou
- $Z^1 = S$, $Z^2 = O$, $R^1 = CH(CO_2Et)_2$ et $R^2 = Et$.

INTERNATIONAL SEARCH REPORT

Intern. Appl. No.

PCT/FR 98/01316

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F293/00 C08F2/38 C07C329/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2 396 997 A (C. FRYLING) 19 March 1946 see the whole document ---	1
A	EP 0 348 166 A (KURARAY CO., LTD) 27 December 1989 see page 14, line 25-51; claim 1; examples 22,23 ---	1
A	M. OKAWARA ET AL.: "syntheses and photochemical reactions of polymers containing dithiocarbamate and xanthate groups and their model compounds" BULLETIN OF THE TOKYO INSTITUTE OF TECHNOLOGY, no. 78, 1966, page 1-16 XP002049822 JP see example 7 --- -/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search

5 October 1998

Date of mailing of the international search report

20/10/1998

Name and mailing address of the ISA

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Authorized officer

Meulemans, R

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/FR 98/01316

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2396997 A	19-03-1946	NONE	
EP 348166 A	27-12-1989	JP 2018177 C	19-02-1996
		JP 2077478 A	16-03-1990
		JP 7053846 B	07-06-1995
		DE 68914726 D	26-05-1994
		DE 68914726 T	04-08-1994
		US 5186783 A	16-02-1993
		US 5254198 A	19-10-1993
EP 582183 A	09-02-1994	IT 1255775 B	15-11-1995
		DE 69302864 D	04-07-1996

RAPPORT DE RECHERCHE INTERNATIONALE

Deman internationale No
PCT/FR 98/01316

C.(suite) DOCUMENTS CONSIDERES COMME PERTINENTS		
Catégorie	Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents	no. des revendications visées
A	H. SINGER ET AL.: "alpha, omega funktionalisierte oligomere-..." FASERFORSCHUNG UND TEXTIL TECHNIK, vol. 28, no. 9, 1977, pages 435-438, XP002049825 voir page 437, colonne 1 - page 438, colonne 1 ---	1
A	S. SURYAWANSHI ET AL.: "mild and efficient conversion of allylic alcohols to xanthates" SYNTHETIC COMMUNICATIONS, vol. 20, no. 5, 1990, pages 625-632, XP002049823 voir le document en entier ---	1
A	H. YOSHIDA ET AL.: "the conversion of some alkylxanthates to the corresponding trithiocarbonates..." BULLETIN OF THE CHEMICAL SOC. OF JAPAN, vol. 44, 1971, pages 3106-3108, XP002049824 * 3 ème composé du tableau 1 * ---	1
A	EP 0 582 183 A (CONSIGLIO NAZIONALE DELLE RICERCHE) 9 février 1994 voir page 7, ligne 8 voir page 7, ligne 24 -----	1

FORM P1		REPUBLIC OF SOUTH AFRICA PATENTS ACT, 1978 APPLICATION FOR A PATENT AND ACKNOWLEDGEMENT OF RECEIPT (Section 30(1) - Regulation 39)		JOHN & KERNICK P O Box 3511 HALFWAY HOUSE 1685	
The grant of a Patent is hereby requested by the undermentioned applicant(s) on the present application filed in duplicate m50958-1					
21	01	Official Application No 185450	22	Lodging Date 23 June 1998	47 J & K Reference AP 33733 ZA
71	Full name(s) of applicant(s) RHODIA CHIMIE, a legal body organised and existing under the laws of France				
	Address(es) of applicant(s) 25, Quai Paul Doumer, F-92408 - Courbevoie Cedex, France				
54	Title of Invention PROCEDE DE SYNTHESE DE POLYMERES A BLOCS PAR POLYMERISATION RADICALAIRE CONTROLEE				
<input checked="" type="checkbox"/>	The applicant claims priority as set out in the accompanying form P2. The earliest priority claimed is FR 97 07764 23 June 1997				
<input type="checkbox"/>	This application is for a Patent of Addition to Patent Application No.				
<input type="checkbox"/>	This application is a fresh application in terms of S 37 and based on Application No.				
<input type="checkbox"/>	This application is accompanied by:				
<input checked="" type="checkbox"/>	1a A single copy of a provisional specification of pages				
<input type="checkbox"/>	1b Two copies of a complete specification of 62 pages (in the French Language)				
<input type="checkbox"/>	2a Informal drawings of sheets				
<input type="checkbox"/>	2b Formal drawings of sheets				
<input type="checkbox"/>	3. Publication particulars and abstract (form P8 in duplicate)				
<input type="checkbox"/>	4. A copy of Figure of the drawings for the abstract				
<input type="checkbox"/>	5. Assignment of invention (from the Inventors) or other evidence of title				
<input type="checkbox"/>	6. Certified priority documents (documents)				
<input type="checkbox"/>	7. Translation of priority documents (documents)				
<input type="checkbox"/>	8. Assignment of priority rights				
<input type="checkbox"/>	9. A copy of form P2 and the specification of S.A. Patent Application				
<input type="checkbox"/>	10. A declaration and power of attorney on form P3				
<input type="checkbox"/>	11. Request for ante-dating on form P4				
<input type="checkbox"/>	12. Request for classification on form P9				
<input type="checkbox"/>	13a Request for delay of acceptance on form P4				
<input type="checkbox"/>	13b				
74	Address for Service: JOHN & KERNICK, Midrand.				
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> Date <u>23 June 1998</u> </div> <div style="width: 50%; text-align: right;"> <div style="border: 1px solid black; padding: 5px; display: inline-block;"> REGISTRAR OF PATENTS, TRADE MARKS AND COPYRIGHTS 1998-06-23 For the Applicant 23 </div> <div style="border: 1px solid black; padding: 5px; display: inline-block; margin-left: 10px;"> Official date stamp 1998-06-23 </div> </div> </div> <p style="margin-top: 10px;">The duplicate will be returned to the applicant for service as proof of lodging but is not valid unless endorsed with official stamp.</p> <div style="display: flex; justify-content: space-between; margin-top: 10px;"> <div style="width: 45%; text-align: center;"> <div style="border: 1px solid black; padding: 5px; display: inline-block;"> REGISTRAR OF PATENTS, TRADE MARKS AND COPYRIGHTS 1998-06-23 For the Applicant 23 </div> </div> <div style="width: 50%; text-align: right;"> <div style="border: 1px solid black; padding: 5px; display: inline-block;"> REGISTRAR OF PATENTS, TRADE MARKS AND COPYRIGHTS 1998-06-23 For the Applicant 23 </div> </div> </div>					

FORM P7

REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978

JOHN & KERNICK
P O Box 3511
HALFWAY HOUSE
1685

COMPLETE SPECIFICATION

(Section 30(1) - Regulation 28)

21	01	Official Application No	22	Lodging Date	47	J & K Reference
98/5450			23rd June 1998		AP 33733 ZA	
51	International Classification					
71	Full name(s) of applicant(s)					
RHODIA CHIMIE, a legal body organised and existing under the laws of France						
72	Full name(s) of inventor(s)					
BIADATTI, Thibaud;CHARMOT, Dominique;CORPART, Pascale;ZARD, Samir Z;MICHELET, Daniel						
54	Title of invention					
PROCESS FOR SYNTHESIZING BLOCK POLYMERS BY CONTROLLED RADICAL POLYMERIZATION						

I, Roger Walter GRAY MA DPhil CPhys,
translator to RWS Translations Ltd., of Europa House, Marsham
Way, Gerrards Cross, Buckinghamshire, England, hereby declare
that I am conversant with the English and French languages and
am a competent translator thereof. I declare further that to the
best of my knowledge and belief the following is a true and
correct translation of the accompanying documents in the French
language.

Signed this 10th day of July 1998



R. W. GRAY

For and on behalf of RWS Translations Ltd.

**PROCESS FOR SYNTHESIZING BLOCK POLYMERS
BY CONTROLLED RADICAL POLYMERIZATION**

The present invention relates to a novel
5 radical polymerization process for obtaining block
copolymers.

Block polymers are usually prepared by ionic
polymerization. This type of polymerization has the
drawback of only allowing the polymerization of certain
10 types of non-polar monomers, especially styrene and
butadiene, and of requiring a particularly pure
reaction mixture and temperatures which are often below
room temperature so as to minimize parasitic reactions,
and hence of severe operational constraints.

15 Radical polymerization has the advantage of
being easily carried out without having to comply with
excessive purity conditions, and at temperatures
greater than or equal to room temperature. However,
until recently a radical polymerization process
20 allowing block polymers to be obtained did not exist.

Since then, a new radical polymerization
process has been developed, namely "controlled" or
"living" radical polymerization. Controlled radical
polymerization takes place by the growth, by
25 propagation, of macroradicals. These macroradicals,
which have a very short lifetime, recombine
irreversibly by coupling or dismutation. When the
polymerization takes place in the presence of several

comonomers, the compositional variation of the mixture is infinitely slow compared with the lifetime of the macroradical so that the chains have a sequence of random monomer units and not a block-type sequence.

5 Recently, controlled radical polymerization techniques have been developed in which the ends of polymer chains may be reactivated in the form of a radical by homolytic bond (for example, C-O or C-halogen) scission.

10 Controlled radical polymerization therefore has the following distinct characteristics:

1. the number of chains is fixed throughout the duration of the reaction,
2. the chains all grow at the same rate, resulting
15 in:
 - a linear increase in the molecular masses with conversion,
 - a narrow distribution of masses,
3. the average molecular mass is controlled by the
20 monomer/chain-precursor molar ratio, and
4. the possibility of preparing block copolymers.

The controlled character is even more pronounced when the rate of reactivation of the chains into radicals is very much greater than the rate of
25 growth of the chains (propagation). There are cases where this is not always true (i.e. the rate of reactivation of the chains into radicals is greater than or equal to the propagation rate) and conditions 1

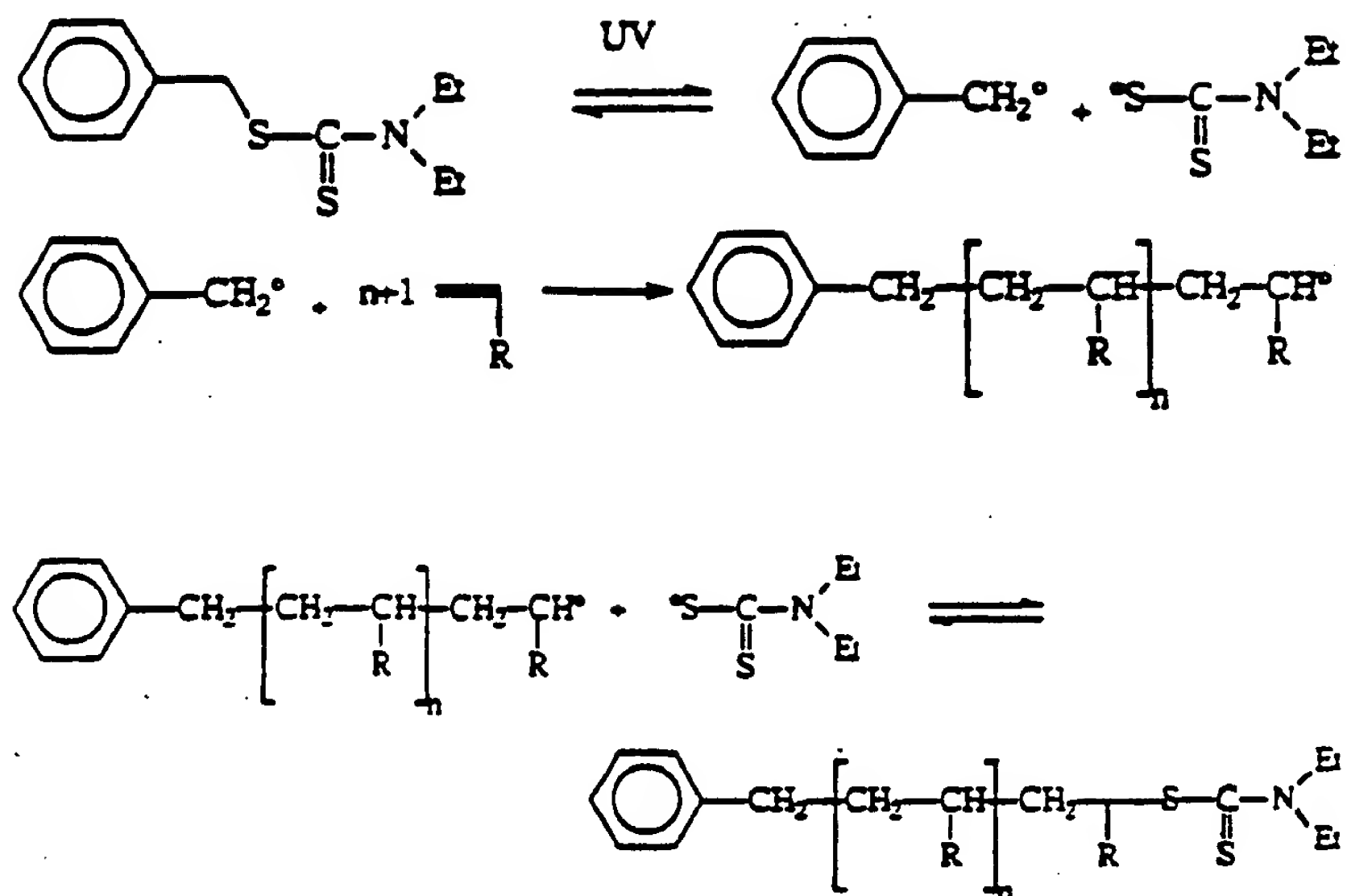
and 2 are not observed, nevertheless it is always possible to prepare block copolymers.

Several approaches have been described for controlling radical polymerization. The most commonly cited consists in introducing, into the mixture, counter radicals which combine reversibly with the growing macroradicals, such as, for example, nitroxyl radicals (Georges et al., *Macromolecules*, 26, 2987, (1993)). This technique is characterized by high temperatures for labilizing the C-O bond.

Another method, called *Atom Transfer Radical Polymerization*, makes use of transition metal salts combined with organic ligands and an initiator generally consisting of an organic halide; control of the polymerization is made possible by the reversibility of the C-halogen bond (K. Matyjaszewski, *PCT WO 96/30421*). One drawback with this polymerization is that a stoichiometric quantity of metal per chain remains.

Otsu (Otsu et al., *Makromol. Chem. Rapid Comm.*, 3, 127-132, (1982), Otsu et al. *ibid*, 3, 123-140, (1982), Otsu et al., *Polymer Bull.*, 7, 45, (1984), *ibid*, 11, 135, (1984), Otsu et al., *J. Macromol. Sci. Chem.*, A21, 961, (1984) and Otsu et al., *Macromolecules*, 19, 2087, (1989)) has shown that certain organic sulphides, particularly dithiocarbamates, allowed chains to be grown in a controlled manner under UV irradiation, according to

the principle:



The principle relies on the photolysis of the C-S bond, which regenerates the carbon macroradical, on the one hand, and the dithiocarbamyl radical, on the other hand. The controlled character of the reaction is due to the reversibility of the C-S bond under UV irradiation. It is thus possible to obtain block copolymers. On the other hand, the equilibrium constant of reaction 1 above is not very large compared with the rate of propagation, this having the consequence of generating relatively broad molecular mass distributions. Thus, the dispersion index ($\text{DI} = M_w/M_n$) is between 2 and 5 (Otsu et al., 25, 7/8, 643-650, (1989)).

Xanthate disulphides and dithiocarbamate disulphides are themselves well known as transfer

agents in conventional radical polymerization in thermal mode and in the presence of an initiator, but no one has hitherto been able to control the polymerization, or even less to produce block copolymers.

Up till now it was known that disulphides (tetraalkylthiuram disulphide, diisopropylxanthate disulphide and mercaptobenzothiazol disulphide) were activatable thermally or under UV irradiation, whereas monosulphides (substituted xanthates, dithiocarbamates) were activatable only under UV irradiation (Roha et al., *Macromol. Symp.*, 91, 81-92, (1995), and Okawara et al., *Bull. of the Tokyo Inst. of Techn.*, No. 78, 1966).

However, controlled radical polymerization making use of a UV irradiation source is very difficult to carry out from an industrial standpoint since the penetration of the UV photons into the polymerization medium is limited, both by absorption phenomena (most of the ethylenic monomers adsorb in the 210 - 280 nm range) and by diffusion phenomena in disperse media (suspension, emulsion).

Moreover, it has been shown (Turner et al., *Macromolecules*, 23, 1856-1859, (1990)) that photopolymerization in the presence of dithiocarbamate generates carbon disulphide and may be accompanied by a loss of polymerization control.

For these reasons, it has thus been sought to develop a technique which can be used to obtain block

copolymers by a process without UV irradiation,
preferably by thermal initiation.

Until the present time, no controlled radical
polymerization system has been able to be demonstrated
5 using dithio compounds in the absence of a UV source.

Controlled radical polymerization has an
advantage over conventional radical polymerization when
it is a question of preparing functionalized low-
molecular-weight chains (reactive telomers). Such
10 polymers are desirable for specific applications such
as, for example, coatings and adhesives.

Thus, when it is attempted to synthesize chains
grafted with, on average, 2 functional comonomers, the
fraction of chains with at most one functional site
15 becomes large when the average degree of polymerization
is less than a threshold value (e.g. 20 or 30).
Controlled radical polymerization makes it possible to
reduce, or even to inhibit, the formation of these
oligomers having zero or one functional site which
20 degrade the performance in terms of application.

One object of the present invention is to
provide a novel controlled radical polymerization
process for the synthesis of block polymers.

Another object of the present invention is to
25 provide a controlled radical polymerization process for
the synthesis of block polymers in the absence of a UV
source.

Another object is to provide a controlled

radical polymerization process for the synthesis of block polymers from all types of monomers.

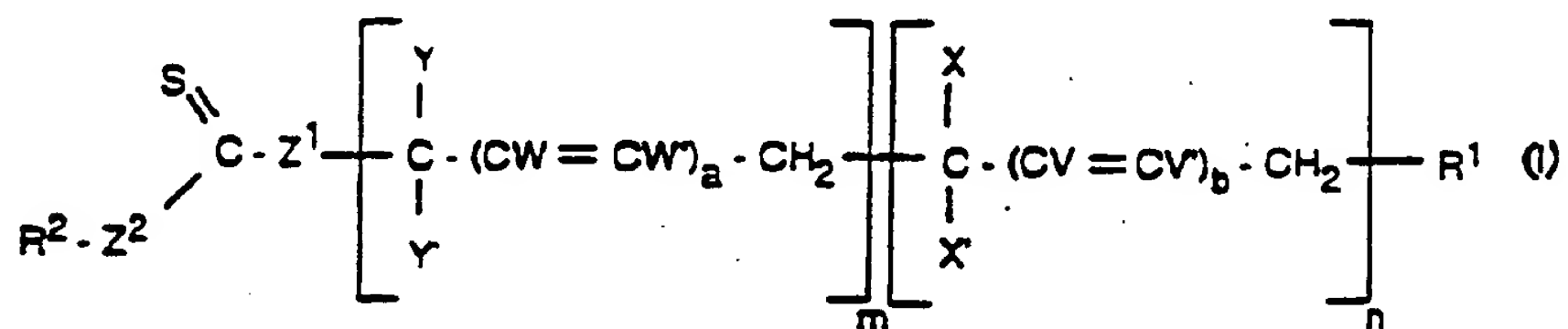
Another object is to provide a controlled radical polymerization process for the synthesis of block polymers containing no metal impurities deleterious to their use.

Another object is to provide a controlled radical polymerization process for the synthesis of block copolymers, the said polymers being chain-end functionalized.

Another object is to provide a controlled radical polymerization process for the synthesis of block polymers and block copolymers having a low polydispersity index.

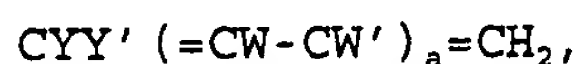
Another object is to provide a controlled radical polymerization process for the synthesis of oligomers in which the number of functional units is constant from chain to chain.

To this end, the invention relates to a process for polymerizing block polymers of general formula (I):

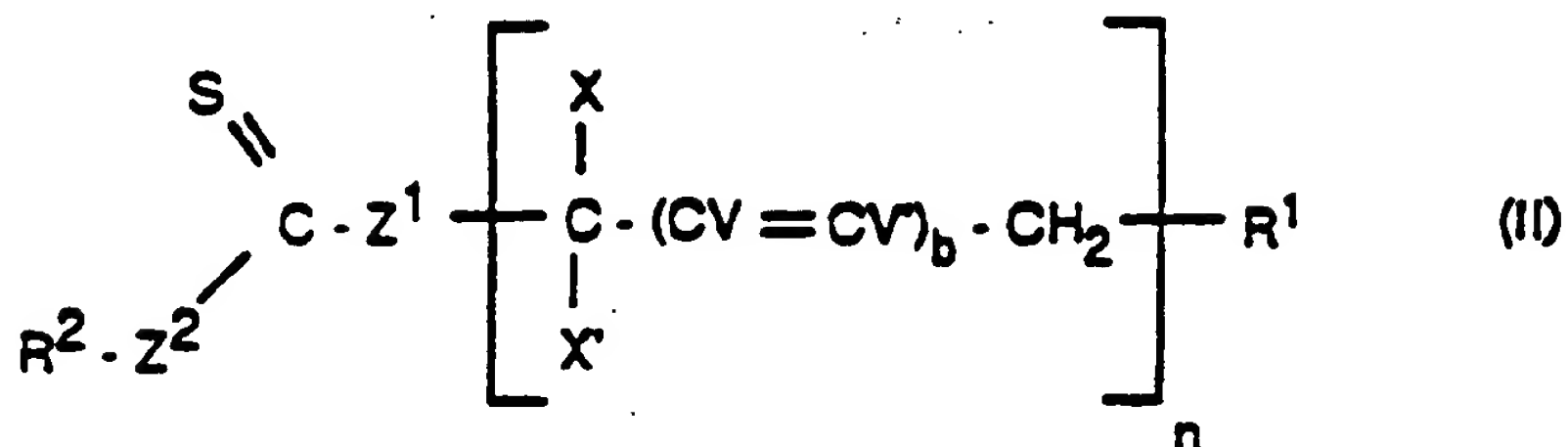


in which process, the following are brought into contact with each other:

- an ethylenically unsaturated monomer of formula:



- a precursor compound of general formula (II):



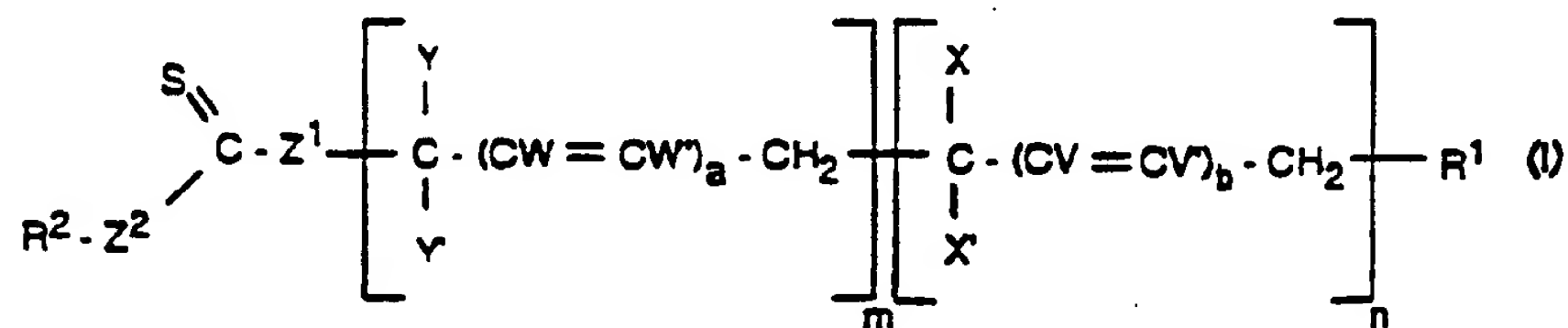
- a radical polymerization initiator.

The invention also relates to the block polymers which can be obtained by the above process.

5 Finally, the invention relates to polymers of general formula (II), the polydispersity index of which is at most 2.

Further details and advantages of the invention will appear more clearly on reading the description and the examples.

10 The invention therefore relates first of all to a process for polymerizing block polymers of general formula (I):



in which:

- 15
- $\text{Z}^1 = \text{S}$ or P ,
 - $\text{Z}^2 = \text{O}$, S or P ,
 - R^1 and R^2 , which are identical or different,

represent:

. an optionally substituted alkyl, acyl, aryl, alkene or alkyne group (i),

or

5 . an optionally substituted, saturated or unsaturated, carbon or aromatic ring (ii),

or

. an optionally substituted, saturated or unsaturated heterocycle (iii),

10 it being possible for these groups and rings (i),

(ii) and (iii) to be substituted with substituted

phenyl groups, substituted aromatic groups, or

groups: alkoxycarbonyl or aryloxy carbonyl ($-\text{COOR}$),

carboxy ($-\text{COOH}$), acyloxy ($-\text{O}_2\text{CR}$), carbamoyl ($-\text{CONR}_2$),

15 cyano ($-\text{CN}$), alkylcarbonyl, alkylarylcarbonyl,

arylcarbonyl, arylalkylcarbonyl, phthalimido,

maleimido, succinimido, amidino, guanidino, hydroxyl

($-\text{OH}$), amino ($-\text{NR}_2$), halogen, allyl, epoxy, alkoxy

($-\text{OR}$), S-alkyl, S-aryl, groups having a hydrophilic

20 or ionic character, such as the alkali metal salts of carboxylic acids, the alkali metal salts of sulphonic acid, polyalkylene oxide chains (PEO, PPO), cationic substituents (quaternary ammonium salts),

R representing an alkyl or aryl group,

25 . a polymer chain,

- V, V', W and W', which are identical or different,

represent: H, an alkyl group or a halogen,

- X, X', Y and Y', which are identical or different,

represent H, a halogen or an R^3 , OR^3 , $OCOR^3$, $NHCOH$,
 OH , NH_2 , NHR^3 , $N(R^3)_2$, $(R^3)_2N^+O^-$, $NHCOR^3$, CO_2H , CO_2R^3 , CN ,
 $CONH_2$, $CONHR^3$ or $CONR^3_2$ group, in which R^3 is chosen
 5 from alkyl, aryl, aralkyl, alkaryl, alkene or
 organosilyl groups, optionally perfluorinated and
 optionally substituted with one or more carboxyl,
 epoxy, hydroxyl, alkoxy, amino, halogen or sulphonic
 groups,

- a and b, which are identical or different, are equal
 10 to 0 or 1,

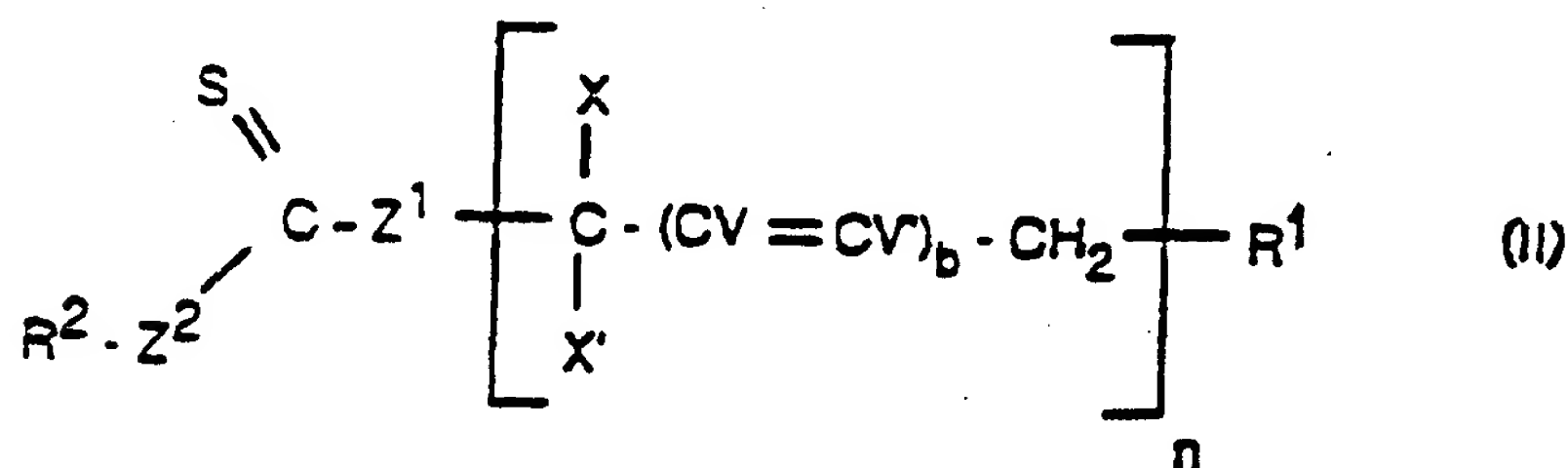
- m and n, which are identical or different, are
 greater than or equal to 1 and, when one or other is
 greater than 1, the individual repeat units are
 identical or different,

15 in which process the following are brought into contact
 with each other:

- an ethylenically unsaturated monomer of formula:



- a precursor compound of general formula (II):



20 - a radical polymerization initiator.

The process therefore consists in bringing
 into contact with each other a radical polymerization

initiator, an ethylenically unsaturated monomer and a precursor of general formula (II).

The radical polymerization initiator may be
 5 chosen from the initiators conventionally used in radical polymerization. These may, for example, be one of the following initiators:

- hydrogen peroxides such as: tert-butyl hydroperoxide, cumene hydroperoxide, tert-butyl
 10 peroxyacetate, tert-butyl peroxybenzoate, tert-butyl peroxyoctoate, tert-butyl peroxyneodecanoate, tert-butyl peroxyisobuturate, lauroyl peroxide, tert-amyl peroxy-pivalate, tert-butyl peroxy-pivalate, dicumyl peroxide, benzoyl peroxide, potassium persulphate and
 15 ammonium persulphate;

- azo compounds such as: 2-2'-azobis(isobutyronitrile), 2,2'-azobis(2-butanenitrile), 4,4'-azobis(4-pentanoic acid), 1,1'-azobis(cyclohexanecarbonitrile), 2-(tert-butylazo)-
 20 2-cyanopropane, 2,2'-azobis[2-methyl-N-(1,1)-bis(hydroxymethyl)-2-hydroxyethyl]propionamide, 2,2'-azobis(2-methyl-N-hydroxyethyl)propionamide, 2-2'-azobis(N,N'-dimethyleneisobutyramidine) dichloride, 2,2'-azobis(2-amidinopropane)dichloride, 2,2'-
 25 azobis(N,N'-dimethyleneisobutyramide), 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide), 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)ethyl]propionamide), 2,2'-

azobis[2-methyl-N-(2-hydroxyethyl)propionamide] and
2,2'-azobis(isobutyramide) dihydrate;

- redox systems including combinations such
as:

5 . mixtures of hydrogen peroxide or alkyl
peroxide, peresters, percarbonates and the like and of
any one of the salts of iron, titanous salts, zinc
formaldehyde sulphonylate or sodium formaldehyde
sulphonylate, and reducing sugars;

10 . alkali-metal or ammonium persulphates,
perborate or perchlorate in combination with an alkali
metal bisulphite, such as sodium metabisulphite, and
reducing sugars;

. alkali-metal persulphate in combination
15 with an arylphosphinic acid, such as benzenephosphonic
acid and other similar acids, and reducing sugars.

The amount of initiator to be used is
determined so that the amount of radicals generated is
at most 20 mol% with respect to the amount of compound
20 (II), preferably at most 5 mol%.

As ethylenically unsaturated monomer, the
monomers chosen from styrene or its derivatives,
butadiene, chloroprene, (meth)acrylic esters, vinyl
esters and vinyl nitriles are more specifically used
25 according to the invention.

Butadiene and chloroprene correspond to the
case in which a and b = 1 in the formulae (I), (II) and
in the formula for the monomer given above.

"(Meth)acrylic esters" should be understood to mean esters of acrylic acid and of methacrylic acid with hydrogenated or fluorinated C₁-C₁₂, preferably C₁-C₈, alcohols. Among compounds of this type, mention
5 may be made of: methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, tert-butyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate and isobutyl methacrylate.

10 The vinyl nitriles include more particularly those having from 3 to 12 carbon atoms, such as, in particular, acrylonitrile and methacrylonitrile.

 It should be noted that styrene may be replaced, completely or partly, by derivatives such as
15 alpha-methylstyrene or vinyltoluene.

 The other ethylenically unsaturated monomers which can be used, alone or as mixtures, or which can be copolymerized with the above monomers, are, for example:

- 20 - vinyl esters of carboxylic acids, such as vinyl acetate, vinyl versatate and vinyl propionate;
 - vinyl halides;
 - ethylenically unsaturated monocarboxylic and dicarboxylic acids, such as acrylic acid,
25 methacrylic acid, itaconic acid, maleic acid and fumaric acid, and monoalkyl esters of dicarboxylic acids of the type mentioned with alkanols preferably having from 1 to 4 carbon atoms and their N-substituted

derivatives;

- amides of unsaturated carboxylic acids, such as acrylamide, methacrylamide, N-methylolacrylamide or methacrylamide, and

5 N-alkylacrylamides;

- ethylenic monomers containing a sulphonic acid group and its ammonium or alkali metal salts, for example vinylsulphonic acid, vinylbenzenesulphonic acid, alpha-acrylamidomethylpropanesulphonic acid and
10 2-sulphoethylene methacrylate;

- amides of vinylamine, especially vinylformamide or vinylacetamide; and

- unsaturated ethylenic monomers containing a secondary, tertiary or quaternary amino group, or a
15 heterocyclic group containing nitrogen, such as, for example, vinylpyridines, vinylimidazole, aminoalkyl (meth)acrylates and aminoalkyl (meth)acrylamides such as dimethylaminoethyl acrylate or methacrylate, di-tert-butylaminoethyl acrylate or methacrylate and
20 dimethylaminomethylacrylamide or dimethylaminomethacrylamide. Likewise, it is possible to use zwitterionic monomers such as, for example, sulphopropyl(dimethyl)aminopropyl acrylate.

In order to prepare the copolymers of formula
25 (I) for which $Y = H$ and $Y' = NH_2$, it is preferred to use as ethylenically unsaturated monomers the amides of vinylamine, for example vinylformamide or vinylacetamide. The copolymer obtained is then

hydrolysed to acid or basic pH.

In order to prepare the copolymers of formula (I) for which $Y = H$ and $Y' = OH$, it is preferred to use as ethylenically unsaturated monomers vinyl esters of carboxylic acid such as, for example, vinyl acetate. The copolymer obtained is then hydrolysed to acid or basic pH.

The types and amounts of copolymerizable monomers employed according to the present invention vary depending on the particular final application for which the block polymer is intended. These variations are well known and may be easily determined by those skilled in the art.

In order for the polymer of general formula (I) to be a block polymer, the "precursor" compound of general formula (II) must be a polymer.

Thus, n is greater than or equal to 1, preferably greater than or equal to 6. The monomer units of this polymer may be identical or different.

According to the preferred embodiment of the invention, in the formula (II) for the precursor compounds, Z^1 is a sulphur atom and Z^2 is an oxygen atom; these compounds are therefore chain-end functionalized by alkyl xanthates.

Preferably, in the formula (II) for the precursor compounds, R^1 represents:

- a group of formula $CR'^1R'^2R'^3$ in which:

. R'^1 , R'^2 and R'^3 represent groups (i), (ii) or (iii)

as defined above or

. $R'^1 = R'^2 = H$ and R'^3 is an aryl, alkene or alkyne group,

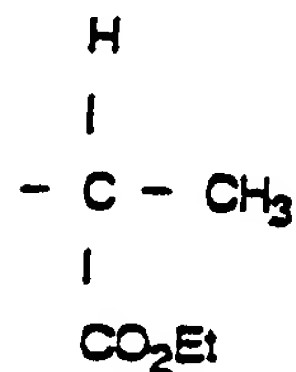
- or a $-COR'^4$ group in which R'^4 represents a group (i),

5 (ii) or (iii) as defined above.

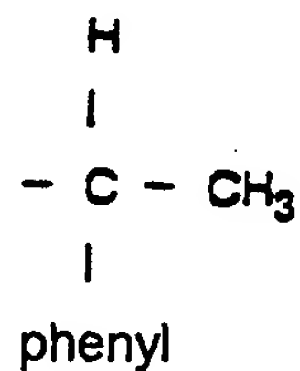
Likewise, in the formula (II) for the precursor compounds, R^2 preferably represents a group of formula: $-CH_2R'^5$, in which R'^5 represents H or a group (i), (ii) or (iii) with the exception of aryl, alkyne
10 and alkene groups.

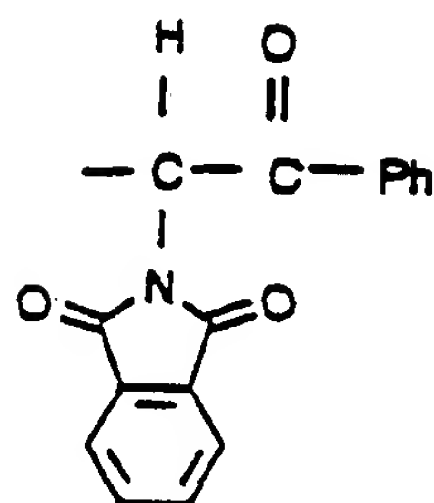
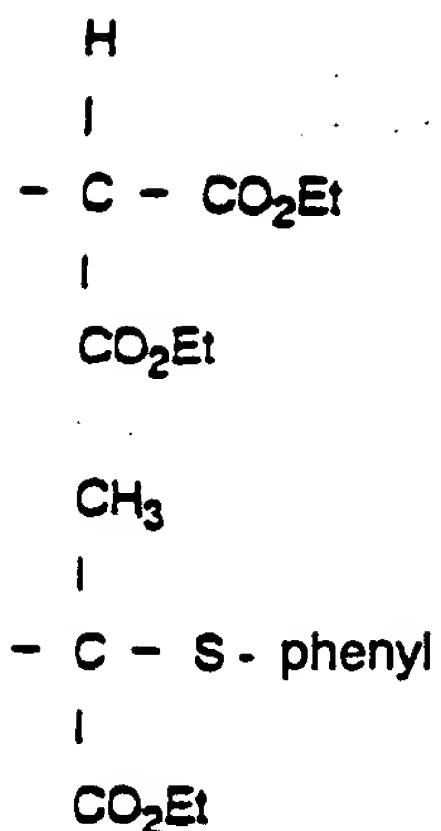
The most interesting results have been obtained for compounds of formula (II) when Z^1 is a sulphur atom, Z^2 is an oxygen atom, R^2 is an ethyl or phenyl group and R^1 is a group chosen from:

15



20



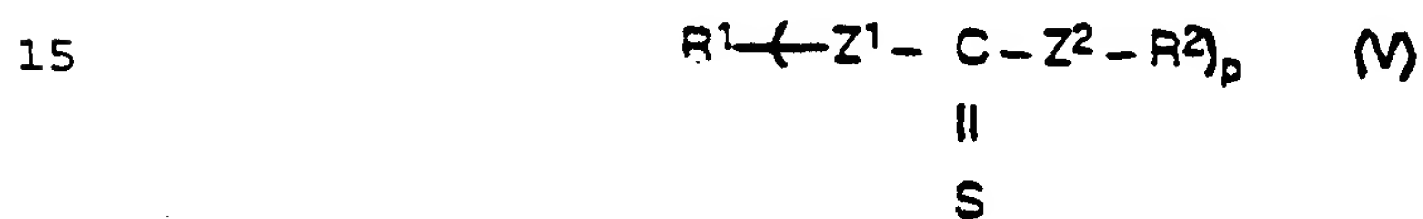
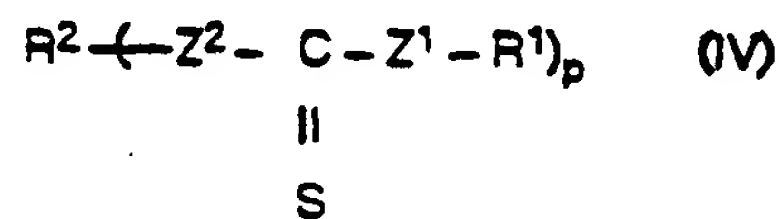
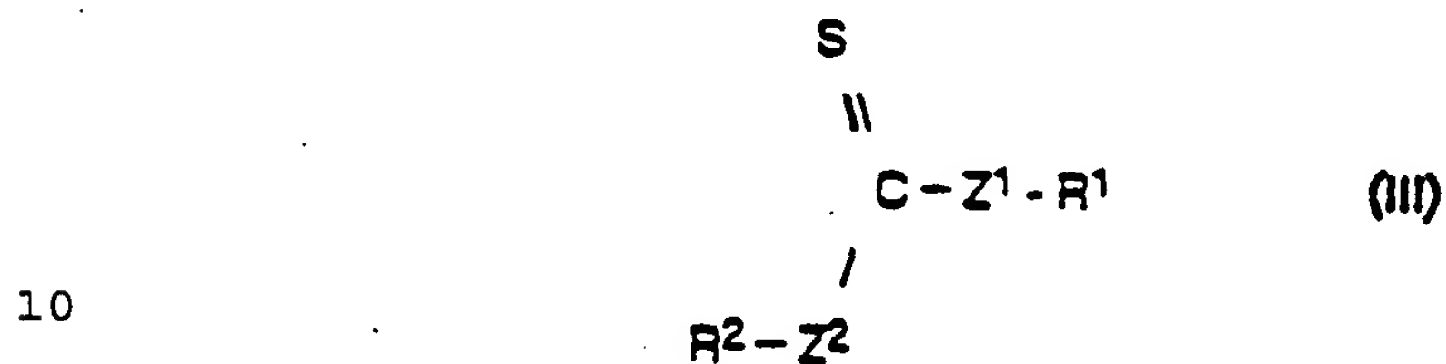


The R^1 group may also represent a polymer chain coming from a radical or ionic polymerization or coming from a polycondensation.

The compounds (II) particularly preferred are styrene ($Y' = \text{H}$, $Y = \text{C}_6\text{H}_5$, $b = 0$), methyl acrylate ($Y' = \text{H}$, $Y = \text{COOMe}$, $b = 0$), ethyl acrylate ($Y' = \text{H}$, $Y = \text{COOEt}$, $b = 0$), butyl acrylate ($Y' = \text{H}$, $Y = \text{COOBu}$, $b = 0$), tert-butyl acrylate ($Y' = \text{H}$, $Y = \text{COOtBu}$, $b = 0$), vinyl acetate ($Y' = \text{H}$, $Y = \text{OCOMe}$, $b = 0$) and acrylic acid ($Y' = \text{H}$, $Y = \text{COOH}$, $b = 0$) homopolymers, for which:

- $Z^1 = \text{S}$, $Z^2 = \text{O}$, $R^1 = \text{CHCH}_3(\text{CO}_2\text{Et})$ and $R^2 = \text{Et}$, or
- $Z^1 = \text{S}$, $Z^2 = \text{O}$, $R^1 = \text{CH}(\text{CO}_2\text{Et})_2$ and $R^2 = \text{Et}$.

This precursor polymer (II) may come from the radical polymerization of an ethylenically unsaturated monomer of formula: $CXX' (=CV-CV')_p=CH_2$ by bringing the said monomer into contact with a radical polymerization
 5 initiator and a compound of general formula (III), (IV) or (V):



p being between 2 and 10, preferably between 2 and 5.

In this synthesis, the radical polymerization
 20 initiators and the ethylenically unsaturated monomers are of the type previously mentioned.

With regard to the compounds of general formulae (III), (IV) or (V), the symbols R^2 , Z^2 , R^1 and Z^1 have the same meaning as previously. As regards their
 25 symbols, the preferred ones are the same as previously.

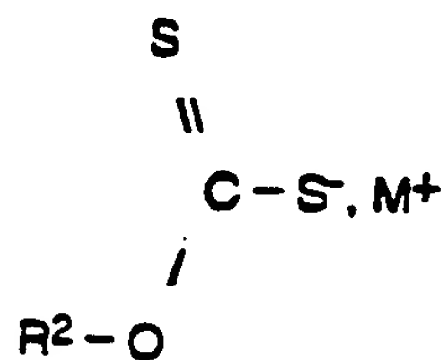
Thus, the preferred compounds of general formula (III) are ethyl α -(O-ethylxanthyl)propionate ($Z^1 = S$, $Z^2 = O$, $R^1 = CH(CH_3)(CO_2Et)$, $R^2 = Et$) and

[1-(O-ethylxanthyl)malonate ($Z^1 = S$, $Z^2 = O$, $R^1 = CH(CO_2Et)_2$, $R^2 = Et$).

Among compounds of formula (IV), those for which R^2 is the $-(CH_2)_q$ -group or a polyether group
 5 $-(CHR-CH_2-O)_q-CHR-CH_2-$, with q between 2 and 10, are preferred.

Among the compounds of formula (V), those for which R^1 is the group $-CH_2$ -phenyl- CH_2- or the group $-CHCH_3CO_2CH_2CH_2CO_2CHCH_3-$ are preferred.

10 The compounds of formulae (III), (IV) and (V) are readily accessible. Those for which Z^1 is a sulphur atom and a Z^2 is an oxygen atom, called alkyl xanthates, may in particular be obtained by reaction between a xanthate salt, such as an alkali metal salt of the
 15 type:

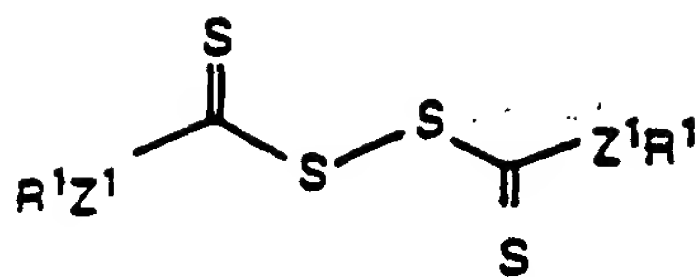


20

and a halogenated derivative of the type: $Hal-R^1$, with Hal chosen from Cl , Br or I .

The compounds of formulae (III), (IV) and (V), in which Z^1 is S , may also be obtained by the
 25 process in which the following are mixed and heated:

- a disulphide (S) compound of formula (A):



5 - and a diazo (N) compound of formula (B):



The complete process of synthesizing a block
 10 polymer of formula (I) according to the invention may
 therefore consist in:

(1) synthesizing a polymer by bringing into
 contact with each other an ethylenically unsaturated
 monomer of formula $(\text{CXX}' (= \text{CV}-\text{CV}'))_b = \text{CH}_2$, a radical
 15 polymerization initiator and a compound of formula
 (III), (IV) or (V), and

(2) using the polymer obtained as precursor
 of general formula (II) in order to prepare a diblock
 polymer by bringing it into contact with a new
 20 ethylenically unsaturated monomer of formula:
 $\text{CYY}' (= \text{CW}-\text{CW}')_a = \text{CH}_2$ and a radical polymerization
 initiator.

This step (2) may be repeated as many times
 as desired using new monomers to synthesize new blocks
 25 and to obtain a multiblock polymer.

As indicated previously, for the preparation
 of precursors of formula (II) for which $\text{X} = \text{H}$ and $\text{X}' =$
 NH_2 (step (1) defined above), it is preferred to use, as

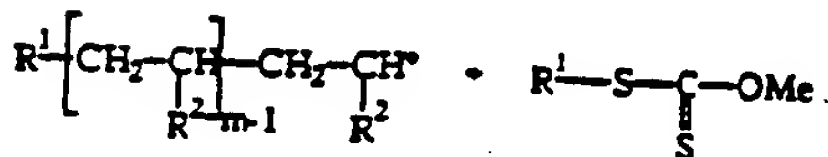
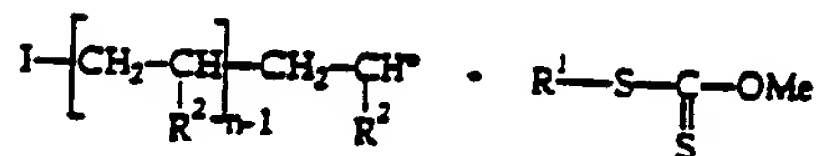
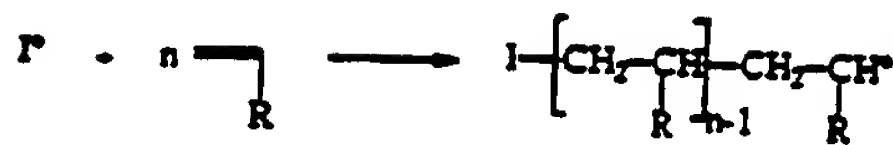
ethylenically unsaturated monomers, amides of vinylamine, for example vinylformamide or vinylacetamide. The polymer obtained is then hydrolysed to acid or basic pH.

5 Likewise, for the preparation of precursors of formula (II) for which $X = H$ and $X' = OH$, it is preferred to use vinyl esters of carboxylic acids, such as vinyl acetate for example, as ethylenically unsaturated monomers. The polymer obtained is then
10 hydrolysed to acid or basic pH.

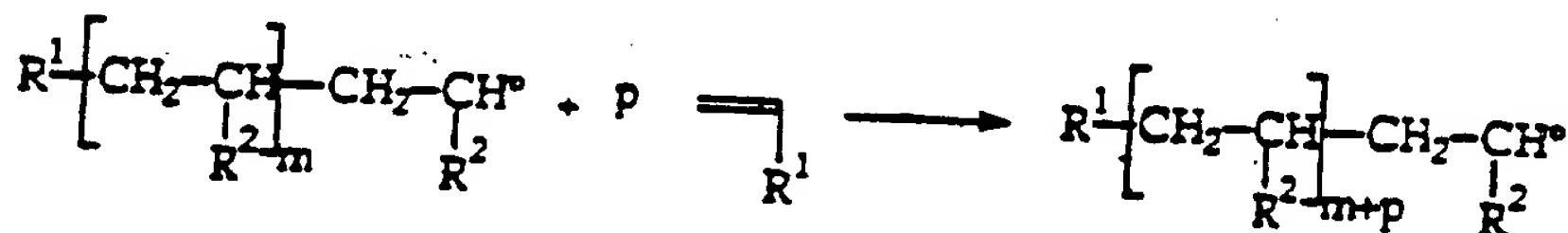
Without thereby excluding any other reaction scheme, the presumed action mechanism of the polymerization is illustrated below in the case of a xanthate-type precursor compound of formula (II).

15

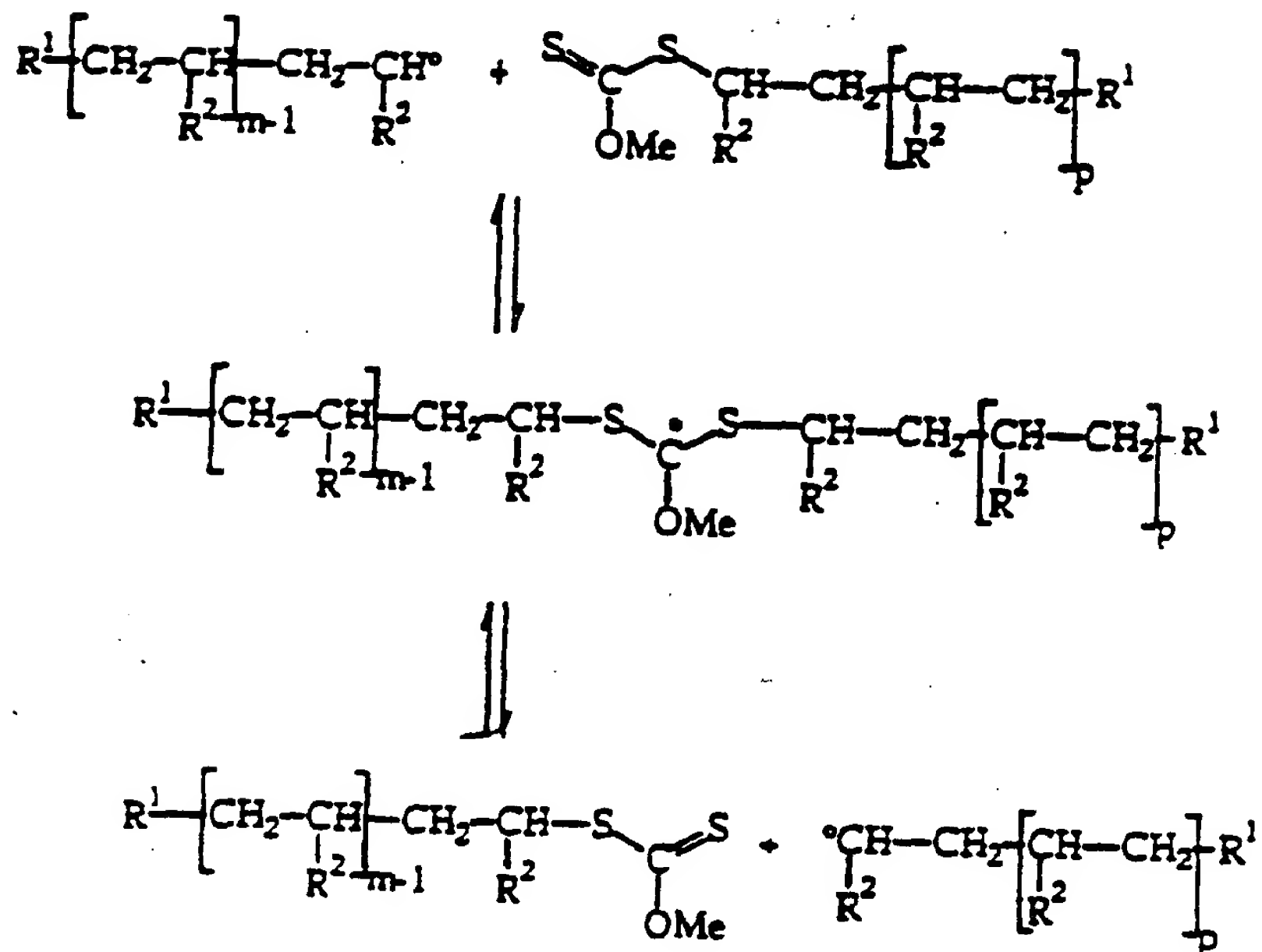
1. Initiation of the polymerization:



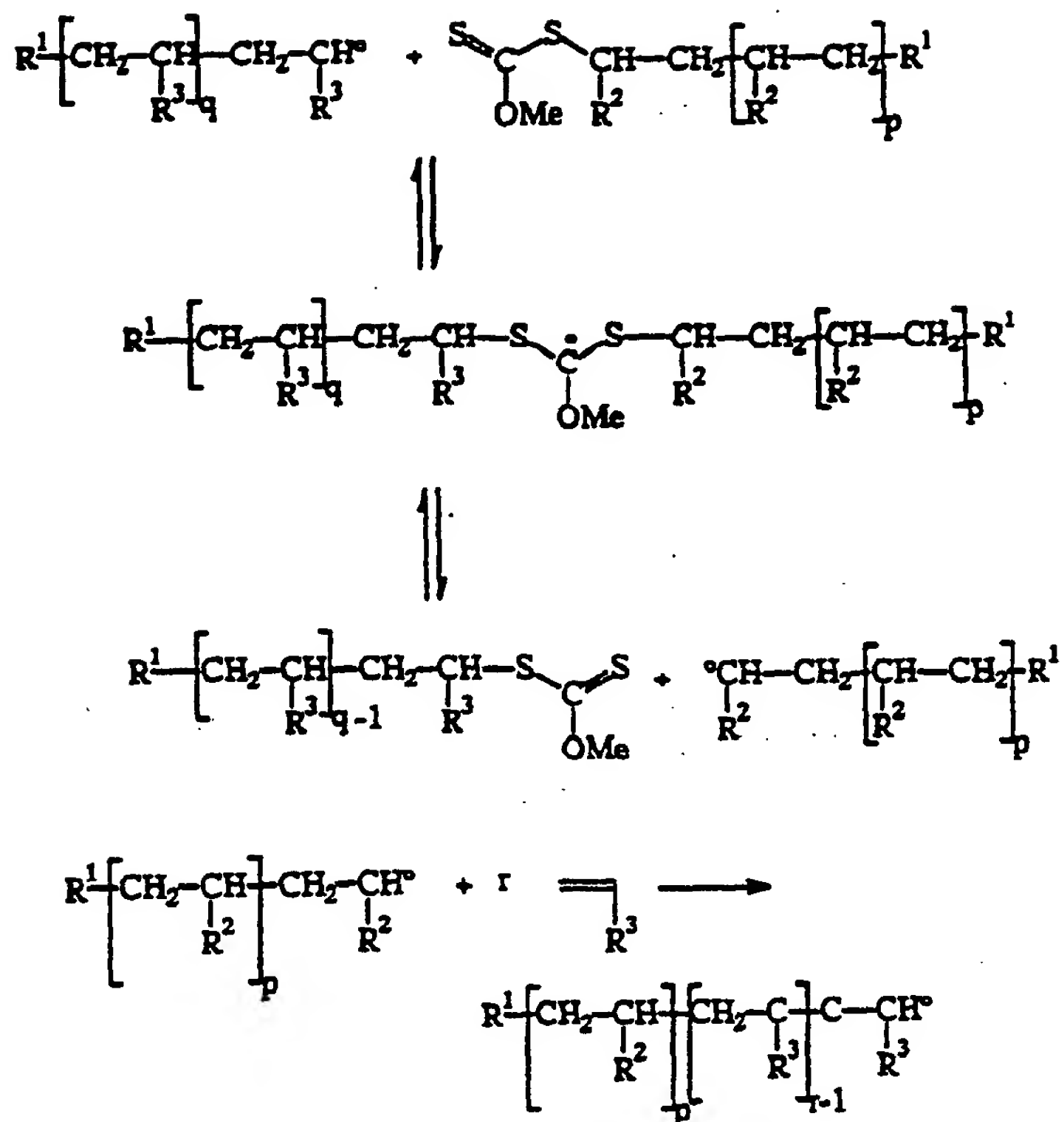
2. Chain growth



3. D generative chain transfer



The degenerative chain transfer reaction makes it possible to react a "dormant" chain carrying the xanthate unit at its end into a macroradical. This unit may grow by propagation and again be added onto a xanthate chain end, and fragment. When the xanthate exchange rate is at least as great as the propagation rate the chains will then grow according to a controlled process. When the $\text{CH}_2=\text{CHR}^2$ monomer is completely consumed, a second monomer of a different type, $\text{CH}_2=\text{CHR}^3$, is introduced into the mixture and then block copolymers of general formula (I) are obtained:



According to this principle, the invention therefore also relates to a process for preparing multiblock polymers, in which the implementation of the process previously described is repeated at least once, using:

- different monomers from those of the previous implementation, and
- instead of the precursor compound of formula (II), the block polymer coming from the previous implementation.

If the implementation is repeated once, a triblock polymer will be obtained, if it is repeated

twice, a "quadriblock" polymer will be obtained, and so on. In this way, at each new implementation, the product obtained is a block polymer having an additional polymer block.

5 Therefore, in order to prepare multiblock polymers, the process consists in repeating, several times, the implementation of the preceding process on the block polymer coming from each previous implementation using different monomers.

10 According to this method of preparing multiblock polymers, when it is desired to obtain homogeneous block polymers without a composition gradient, and if all the successive polymerizations are carried out in the same reactor, it is essential for
15 all the monomers used in one step to have been consumed before the polymerization of the next step starts, therefore before the new monomers are introduced.

 The compounds of formula (IV) and (V) are particularly advantageous as they allow a polymer chain
20 to be grown on at least two active sites. With this type of compound, it is possible to save on polymerization steps in order to obtain an n-block copolymer.

 Thus, if $p = 2$ in the formula (IV) or (V),
25 the first block is obtained by the polymerization of a monomer M1 in the presence of the compound of formula (IV) or (V). This first block may then grow at each of its ends by the polymerization of a second monomer M2.

A triblock copolymer is obtained, this triblock polymer can itself grow at each of its ends by the polymerization of a third monomer M3. Thus, a "pentablock" copolymer is obtained in only three steps.

5 If p is greater than 2, the process makes it possible to obtain homopolymers or block copolymers whose structure is "multi-branched" or "hyperbranched".

 The polymerization may be carried out in bulk, in solution or in emulsion. Preferably, it is
10 carried out in emulsion.

 Preferably, the process is carried out semi-continuously.

 The temperature may vary between ambient temperature and 150°C, depending on the nature of the
15 monomers used.

 In general, during the polymerization, the instantaneous polymer content with respect to the instantaneous amount of monomer and polymer is between 50 and 99% by weight, preferably between 75 and 99%,
20 even more preferably between 90 and 99%. Polymer is understood to mean either the compound of formula (I) for synthesizing a block copolymer or the compound of formula (II) for synthesizing the precursor polymer. This content is maintained, in a known manner, by
25 controlling the temperature, the rate of addition of the reactants and of the polymerization initiator.

 The process according to the invention has the advantage of resulting in block polymers having a

low polydispersity index.

It also makes it possible to control the molecular mass of the polymers.

The invention therefore also relates to the block polymers which can be obtained by the above process.

In general, these polymers have a polydispersity index of at most 2, preferably of at most 1.5.

These results are especially obtained for block polymers of formula (I) which is chain-end functionalized by the alkyl xanthate group.

These polymers correspond to the polymers of general formula (I) for which Z^1 is a sulphur atom and Z^2 is an oxygen atom.

The preferred block polymers are those having at least two polymer blocks chosen from the following combinations:

- polystyrene/polymethyl acrylate
- polystyrene/polyethyl acrylate,
- polystyrene/poly(tert-butyl acrylate),
- polyethyl acrylate/polyvinyl acetate,
- polybutyl acrylate/polyvinyl acetate,
- poly(tert-butyl acrylate)/polyvinyl acetate,
- polyethyl acrylate/poly(tert-butyl acrylate),
- polybutyl acrylate/polybutyl acrylate,
- polyacrylic acid/polyvinyl alcohol.

According to a preferred mode, the polymers have at least two polymer blocks chosen from the above combinations and are of general formula (I) in which:

- $Z^1 = S$, $Z^2 = O$, $R^1 = CHCH_3(CO_2Et)$ and $R^2 = Et$, or
- 5 - $Z^1 = S$, $Z^2 = O$, $R^1 = CH(CO_2Et)_2$ and $R^2 = Et$.

Finally, the process for synthesizing the precursor polymers of general formula (II) also makes it possible to synthesize polymers having a low polydispersity index. In general, these precursor
 10 polymers have a polydispersity index of at most 2, preferably of at most 1.5, especially when these polymers are alkyl-xanthate functionalized polymers (Z^1 being a sulphur atom and Z^2 being an oxygen atom).

Preferably, n is greater than or equal to 6.

15 The compounds (II) particularly preferred are styrene ($Y' = H$, $Y = C_6H_5$, $b = 0$), methyl acrylate ($Y' = H$, $Y = COOMe$, $b = 0$), ethyl acrylate ($Y' = H$, $Y = COOEt$, $b = 0$), butyl acrylate ($Y' = H$, $Y = COOBu$, $b = 0$), tert-butyl acrylate ($Y' = H$, $Y = COOtBu$, $b = 0$),
 20 vinyl acetate ($Y' = H$, $Y = OCOMe$, $b = 0$) and acrylic acid ($Y' = H$, $Y = COOH$, $b = 0$) homopolymers, for which:

- $Z^1 = S$, $Z^2 = O$, $R^1 = CH(CH_3)(CO_2Et)$ and $R^2 = Et$, or
- $Z^1 = S$, $Z^2 = O$, $R^1 = CH(CO_2Et)_2$ and $R^2 = Et$.

The following examples illustrate the
 25 invention without, however, limiting the scope thereof.

EXAMPLES**1. SYNTHESIS OF (alkyl xanthate) PRECURSORS OF FORMULA (III)**

5

**Example 1.1: Synthesis of the ethyl
 α -(O-ethylxanthyl)propionate precursor**

Approximately 1 litre of ethanol and 80 ml of ethyl α -bromopropionate are introduced into a round-bottomed flask. The flask is immersed in an ice bath. Homogenization takes place with stirring and under a flow of nitrogen. When the temperature of the reaction mixture has stabilized, 109 g of potassium O-ethylxanthate are added. The stirring and nitrogen stream are maintained for approximately 4 hours during which the mixture becomes whitish because of the formation of KBr.

When the reaction has reached completion, approximately 1 litre of water is added to the reactor. The mixture becomes clear and yellow. The desired product is extracted from the water-alcohol phase by means of an ether/pentane (1/2) mixture and recovered by vacuum evaporation.

The ^{13}C NMR spectrum gives the following peaks:

171.21; 70.11; 61.62; 47.01; 16.82; 14.04; 13.60.

**Example 1.2: Synthesis of the
[1-(O-ethylxanthyl)ethyl]benzene precursor**

1 litre of ethanol and 80 ml of
(1-bromoethyl)benzene are introduced into a round-
bottomed flask. The flask is immersed in an ice bath.
Homogenization takes place with stirring and under a
5 stream of nitrogen. When the temperature of the
reaction mixture has stabilized, 104 g of potassium
O-ethylxanthate are added. The stirring and stream of
nitrogen are maintained for approximately 4 hours
during which the medium becomes whitish because of the
10 formation of KBr.

When the reaction has reached completion,
approximately 1 litre of water is added to the reactor.
The mixture becomes clear and yellow. The desired
product is extracted from the water-alcohol phase by
15 means of an ether/pentane (1/2) mixture and recovered
by vacuum evaporation.

The ^{13}C NMR spectrum gives the following
peaks: 213.25; 141.73; 128.57; 127.47; 126.49; 69.69;
49.21; 21.70; 13.71.

20

**Example 1.3: Synthesis of the α,α' -
di(O-ethylxanthyl)-p-xylene precursor**

Approximately 1 litre of ethanol and 80 ml of
 α,α' -dichloro-p-xylene are introduced into a round-
25 bottomed flask. The flask is immersed in an ice bath.
Homogenization takes place with stirring and under a
stream of nitrogen. When the temperature of the
reaction medium has stabilized, 184 g of potassium

O-ethylxanthate are added. The stirring and stream of nitrogen are maintained for approximately 4 hours during which the medium becomes whitish because of the formation of KCl.

5 When the reaction has reached completion, approximately 1 litre of water is added to the reactor. The mixture becomes clear and yellow. The desired product is extracted from the water-alcohol phase by means of a dichloromethane/ether/pentane (1/1/2)
10 mixture and recovered by vacuum evaporation.

 The ^{13}C NMR spectrum gives the following peaks: 135.27; 129.42; 70.23; 40.12; 13.89.

Example 1.4: Synthesis of the

15 α -(O-ethylxanthyl)- α -phthalimidoacetophenone precursor

74 ml of acetone and 12.7 g of α -bromo- α -phthalimidoacetophenone are introduced into a round-bottomed flask. The mixture is homogenized with stirring and under a stream of nitrogen. 6.5 g of
20 potassium O-ethylxanthate salt are added. The reaction lasts 5 min, after which the reaction mixture is diluted with distilled water.

 The precipitated solid is filtered, dried and purified by recrystallization in ethanol.

25 The ^{13}C NMR spectrum gives the following peaks: 210.0; 189.2; 166.2; 134.4; 133.8; 133.6; 131.5; 128.7; 128.4; 123.7; 71.6; 61.8; 13.6.

**Example 1.5: Synthesis of the ethyl
 α -(O-ethylxanthyl)- α -phenylthiopropionate precursor**

11 ml of acetone and 2.36 g of potassium
O-ethylxanthate salt are introduced into a round-
5 bottomed flask. The mixture is homogenized with
stirring and under a stream of nitrogen, and then a
solution of ethyl α -chloro- α -phenolthiopropionate
(1.56 g) in acetone (4 ml) is added drop by drop. The
mixture is stirred for 30 min. The solvent is
10 evaporated. The residue [lacuna] diluted with ether and
then washed in water.

The organic phase is separated and dried on
sodium sulphate. The product is recovered after
concentration in vacuo and purification by
15 chromatography on silica.

The ^{13}C NMR spectrum gives the following
peaks: 211.3; 168.8; 137.6; 130.4; 129.0; 128.9; 69.72;
62.99; 62.13; 25.56; 13.80; 13.37.

20 **Example 1.6: Synthesis of the
(O-ethylxanthyl)malonate precursor**

50 ml of acetone and 4 ml of
diethylchloromalonate are introduced into a round-
bottomed flask. The mixture is homogenized with
25 stirring and under a stream of nitrogen and 4.4 g of
potassium O-ethylxanthate salt is added. The reaction
lasts 1 hour, after which the reaction medium is
diluted with 20 ml of water.

The product is extracted from the phase thus obtained by 50 ml of ether, and then purified by flash chromatography.

The ^{13}C NMR spectrum gives the following
5 peaks: 210.3; 165.2; 71.0; 62.8; 56.4; 14.0; 13.6.

**Example 1.7: Synthesis of the ethyl
 α -(O-phenylethylxanthyl)- α -phenylthiopropionate
precursor**

10 20 ml of acetone and 5.58 g of potassium
O-phenylethylxanthate are introduced into a round-
bottomed flask. The mixture is homogenized with
stirring and under a stream of nitrogen, then the
temperature is lowered to 0°C.

15 A solution of ethyl α -chloro-
 α -phenylthiopropionate (6.15 g) in acetone (20 ml) is
added to the flask drop by drop. The mixture is stirred
for 2 hours.

Next, the solvent is evaporated. The residue
20 is diluted with ether, washed firstly with water and
then with a saturated aqueous solution of NaCl. The
organic phase is separated and dried on sodium
sulphate.

The product is recovered in the form of white
25 crystals after evaporation and recrystallization in
ether at room temperature.

The ^{13}C NMR spectrum gives the following
peaks: 211.27; 168.82; 130.42; 69.72; 62.13; 25.56;

13.80; 13.37.

**Example 1.8: Synthesis of ethyl
 α -(O-phenylethylxanthyl)- α -phenylethanoate precursor**

5 1 equivalent of phenylethyl alcohol
(16.78 ml) in solution in 150 ml of THF is introduced
into a round-bottomed flask after which is added 1
equivalent of NaH (5.68 g) at 0°C.

10 After 2 hours of stirring, 1 equivalent of CS₂
(8.48 ml) is added.

 After stirring overnight at room temperature,
the solution is filtered. The salt is washed with
pentane and then dried. It is isolated quantitatively
in the form of a yellow powder, 1.09 g of which are
15 dissolved in 5 ml of acetone. The solution is cooled to
0°C.

 1 equivalent (0.99 g) of ethyl
 α -chlorophenylethanoate is added. The solution is
stirred for 3 hours at room temperature.

20 Next, it is extracted with ether, dried on
magnesium sulphate and concentrated in vacuo.

 1.62 g of ethyl α -(O-phenylethylxanthyl)-
 α -phenylethanoate is recovered. The overall reaction
yield is 90%.

25

**Example 1.9: Synthesis of the
(O-ethylxanthyl)isobutyronitrile precursor**

10 ml of bis(O-ethyl)xanthate (2.42 g) is dissolved in 36 ml of hexane in a 100 ml round-bottomed flask provided with a refrigerant and under an inert atmosphere of argon.

5 The solution is heated for 15 min and then 1 equivalent of azobis(isobutyronitrile) (AIBN) (1.64 g) is added. 0.5 equivalent of AIBN (0.82 g) is added after two and a half hours.

 The solution is dried under vacuum. The
10 product is purified by chromatography and isolated. The yield is 77%.

**Example 1.10: Synthesis of the ethyl
(O-neopentylxanthyl)malonate precursor**

15 1 equivalent of neopentyl alcohol (2.15 ml) in solution in 30 ml of THF is introduced into a round-bottomed flask. 1 equivalent of NaH (0.81 g) is then added at 0°C.

 After two hours of stirring, 1 equivalent of
20 CS₂ (1.21 ml) is added.

 After stirring overnight at room temperature, the solution is filtered. The salt is washed with pentane and then dried. It is isolated quantitatively in the form of a yellow powder, 1.86 g of which is
25 dissolved in 10 ml of acetone. The solution is cooled to 0°C.

 1 equivalent of ethylchloromalonate (1.61 ml) in 5 ml of acetone is added. The solution is stirred

for 4 hours at room temperature. It is then hydrolysed and extracted with ether. It is then dried on magnesium sulphate and concentrated in vacuo.

After purification by chromatography, 2.08 g
5 of product is isolated. The yield is 65%.

**Example 1.11: Synthesis of the ethyl
(O-isobornylxanthyl)malonate precursor**

15.4 g of isoborneol in solution in 200 ml of
10 THF are introduced into a round-bottomed flask. The solution is treated with 1 equivalent of NaH at 0°C then, after 2 hours of stirring, 6 ml of CS₂ are added.

The solution is stirred overnight at room temperature and then filtered. The salts are then
15 washed with ether. The filtrate is concentrated. It is taken up in pentane and filtered. Finally, it is dried in order to obtain the sodium salt quantitatively.

5.04 g of this salt are dissolved in 40 ml of acetone. The solution is cooled to 0°C. 3.08 ml of
20 ethylchloromalonate are added. The solution is stirred for one hour at 0°C. Next, it is hydrolysed, extracted with ether and then dried on magnesium sulphate and concentrated in vacuo.

After purification by chromatography on
25 silica, 5.92 g of product are obtained. The yield is 80%.

**Exempl 1.12: Synthesis of the
(O-isopropylxanthyl)valeronitrile precursor**

0.336 g of azobisvaleronitrile and 0.27 g of
bis(O-isopropyl)xanthate are dissolved in dioxane. The
5 temperature is raised to 101°C.

After 12 hours of stirring, the solvent is
evaporated and the residue purified by chromatography
on silica.

The product is obtained with a 60% yield.

10

**EXAMPLES 2 - SYNTHESIS OF THE PRECURSORS OF FORMULA
(II) (homopolymers)**

Example 2.1: Styrene homopolymer

15

1 mmol of ethyl α -(O-ethylxanthyl)propionate
(0.222 g) and 40 mmol of styrene (4.16 g) are
introduced into a 10 ml round-bottomed flask. The
temperature is raised to 125°C and 0.03 mmol of lauroyl
peroxide (12.8 mg) are added.

20

The polymerization lasts 9 hours, after which
several additions of initiator are made:

- 0.02 mmol after two hours,
- 0.02 mmol after four hours,
- 0.01 mmol after six hours,
- 25 - 0.01 mmol after eight hours.

The polymer is recovered by precipitation in
methanol and analysed by GPC in a THF medium and in
polystyrene equivalents (see Table 9).

Exempl 2.2: Styren homopolymer

1 mmol of [1-(O-ethylxanthyl)ethyl]benzene
(0.226 g) and 40 mmol of styrene (4.16 g) are
introduced into a 10 ml round-bottomed flask. The
5 temperature is raised to 90°C and 0.02 mmol of lauroyl
peroxide (8.52 mg) are added.

The polymerization lasts 12 hours, during
which several additions of initiator are made:

- 0.01 mmol after two hours,
- 10 - 0.01 mmol after four hours,
- 0.01 mmol after six hours,
- 0.01 mmol after eight hours,
- 0.01 mmol after ten hours.

The polymer is recovered by precipitation in
15 methanol and analysed by GPC in a THF medium and in
polystyrene equivalents (see Table 9).

Example 2.3: Styrene homopolymer

1 mmol of α,α' -di(O-ethylxanthyl)-p-xylene
20 (0.346 g) and 40 mmol of styrene (4.16 g) are
introduced into a 10 ml round-bottomed flask. The
temperature is raised to 90°C and 0.02 mmol of lauroyl
peroxide (8.52 mg) are added.

The polymerization lasts 15 hours, during
25 which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,

- 0.01 mmol after eight hours,
- 0.01 mmol after twelve hours,
- 0.01 mmol after fourteen hours.

The polymer is recovered by precipitation in methanol and analysed by GPC in a THF medium and in polystyrene equivalents (see Table 9).

Example 2.4: Styrene homopolymer

1 mmol of α -(O-ethylxanthyl)-
 α -phthalimidoacetophenone (0.385 g) and 40 mmol of styrene (4.16 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 90°C and 0.02 mmol of lauroyl peroxide (8.52 mg) are added.

The polymerization lasts 15 hours, during which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,
- 0.01 mmol after eight hours,
- 0.01 mmol after twelve hours,
- 0.01 mmol after fourteen hours.

The polymer is recovered by precipitation in methanol and analysed by GPC in a THF medium and in polystyrene equivalents (see Table 9).

25

Example 2.5: Styrene homopolymer

1 mmol of ethyl α -(O-ethylxanthyl)-
 α -phenylthiopropionate (0.33 g) and 40 mmol of styrene

(4.16 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 90°C and 0.02 mmol of lauroyl peroxide (8.52 mg) are added.

The polymerization lasts 15 hours, during
5 which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,
- 0.01 mmol after eight hours,
- 10 - 0.01 mmol after twelve hours,
- 0.01 mmol after fourteen hours.

The polymer is recovered by precipitation in methanol and analysed by GPC in a THF medium and in polystyrene equivalents (see Table 9).

15

Example 2.6: Methyl acrylate homopolymer

1 mmol of ethyl α -(O-ethylxanthyl)propionate (0.222 g), 40 mmol of methyl acrylate (MeA) (3.44 g) and 3.5 ml of toluene are introduced into a 10 ml
20 round-bottomed flask. The temperature is raised to 100°C and 0.035 mmol of lauroyl peroxide (14.9 mg) are added. The polymerization lasts 15 hours, during which several additions of initiator are made:

- 0.02 mmol after two hours,
- 25 - 0.02 mmol after six hours,
- 0.02 mmol after ten hours.

The polymer is recovered by evaporating, under high vacuum, the solvent and the traces of

residual monomers and is analysed by GPC in THF medium and polystyrene equivalents (see Table 9).

Example 2.7: Methyl acrylate homopolymer

5 1 mmol of ethyl α -(O-ethylxanthyl)propionate (0.222 g) and 40 mmol of methyl acrylate (3.44 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 80°C and 0.03 mmol of lauroyl peroxide (12.8 mg) are added.

10 The polymerization lasts 45 min.

 The polymer is recovered by evaporating, under high vacuum, the solvent and the traces of residual monomers. It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

15

Example 2.8: Methyl acrylate homopolymer

 1 mmol of ethyl α -(O-ethylxanthyl)propionate (0.222 g) and 80 mmol of methyl acrylate (6.88 g) are introduced into a 10 ml round-bottomed flask. The
20 temperature is raised to 80°C and 0.02 mmol of lauroyl peroxide (8.52 mg) are added. The polymerization lasts 45 min.

 The polymer is recovered by evaporating, under high vacuum, the traces of residual monomers. It
25 is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.9: Methyl acrylate homopolymer

1 mmol of α -(O-ethylxanthyl)-
 α -phthalimidoacetophenone (0.385 g) and 40 mmol of
methyl acrylate (3.44 g) are introduced into a 10 ml
5 round-bottomed flask. The temperature is raised to 80°C
and 0.02 mmol of lauroyl peroxide (8.52 mg) are added.
The polymerization lasts 45 min.

The polymer is recovered by evaporating,
under high vacuum, the traces of residual monomers. It
10 is analysed by GPC (see Table 9).

Example 2.10: Ethyl acrylate homopolymer

1 mmol of ethyl α -(O-ethylxanthyl)propionate
(0.222 g) and 40 mmol of ethyl acrylate (EtA) (3.44 g)
15 are introduced into a 10 ml round-bottomed flask. The
temperature is raised to 80°C and 0.02 mmol of lauroyl
peroxide (8.52 mg) are added. The polymerization lasts
6 hours.

The polymer is recovered by evaporating,
20 under high vacuum, the traces of residual monomers. It
is analysed by GPC in THF medium and in polystyrene
equivalents (see Table 9).

Example 2.11: Methyl acrylate homopolymer

25 1 mmol of ethyl α -(O-ethylxanthyl)-
 α -phenylthiopropionate (0.33 g) and 40 mmol of methyl
acrylate (3.44 g) are introduced into a 10 ml round-
bottomed flask. The temperature is raised to 80°C and

0.02 mmol of lauroyl peroxide (8.52 mg) are added.

The polymerization lasts 6 hours.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomers. It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.12: 2-ethylhexyl acrylate homopolymer

10 1 mmol of (O-ethylxanthyl)malonate (0.28 g) and 40 mmol of 2-ethylhexyl acrylate (2EHA) (7.36 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 80°C and 0.02 mmol of lauroyl peroxide (8.52 mg) are added.

15 The polymerization lasts 6 hours.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomers. It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

20

Example 2.13: Vinyl acetate homopolymer

1 mmol of ethyl α -(O-ethylxanthyl)propionate (0.222 g) and 40 mmol of vinyl acetate (MVA) (3.44 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 80°C and 0.02 mmol of lauroyl peroxide (8.52 mg) are added.

The polymerization lasts 8 hours, during which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours.

The polymer is recovered by evaporating,
5 under high vacuum, the traces of residual monomers and
analysed by GPC in THF medium and in polystyrene
equivalents (see Table 9).

Example 2.14: Vinyl acetate homopolymer

10 1 mmol of ethyl α -(O-ethylxanthyl)propionate
(0.222 g) and 40 mmol of vinyl acetate (3.44 g) are
introduced into a 10 ml round-bottomed flask. The
temperature is raised to 80°C and 0.02 mmol of lauroyl
peroxide (8.52 mg) are added.

15 The polymerization lasts 4 hours.

The polymer is recovered by evaporating,
under high vacuum, the traces of residual monomers. It
is analysed by GPC in THF medium and in polystyrene
equivalents (see Table 9).

20

Example 2.15: Styrene homopolymer

1 mmol (3.8 g) of the polymer from Example
2.1, chain-end functionalized by the O-ethylxanthyl
group, and 40 mmol of styrene (4.16 g) are introduced
25 into a 10 ml round-bottomed flask. The temperature is
raised to 90°C and 0.02 mmol of lauroyl peroxide
(8.52 mg) are added. The polymerization lasts 10 hours,
during which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,
- 0.01 mmol after eight hours.

5 The polymer is recovered by precipitation in methanol and analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

 This polymer is a styrene homopolymer, but it was obtained as a diblock copolymer with two
10 polystyrene blocks.

Example 2.16: Styrene homopolymer

 The following are introduced into a 2 l reactor:

- 15 - 0.4 g of sodium bicarbonate,
 - 5.4 g of sodium laury sulphate, and
 - 1020 g of water.

 The temperature is increased to 85°C.

 An aqueous ammonium persulphate solution
20 (1.6 g of water + 0.8 g of ammonium persulphate) is added.

 A mixture containing 400 g of styrene and 2.22 g of ethyl α -(O-ethylxanthyl)propionate is added continuously over a period of 2 hours.

25 The temperature is maintained at 85°C for an additional 1 hour, during which an aqueous ammonium persulphate solution (0.8 g of water + 0.4 g of ammonium persulphate) is introduced.

The polymer obtained is recovered after coagulation of the emulsion and analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

5 **Example 2.17: Styrene homopolymer**

1 mmol of (O-ethylxanthyl)malonate (0.28 g) and 40 mmol of styrene (4.16 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 95°C and 0.03 mmol of lauroyl peroxide (12.8 mg) are
10 added..

The polymerization lasts 10 hours, during which several additions of initiator are made:

- 0.02 mmol after two hours,
- 0.02 mmol after four hours,
- 15 - 0.02 mmol after six hours,
- 0.02 mmol after eight hours.

The polymer is recovered by precipitation in methanol.

It is analysed by GPC in THF medium and in
20 polystyrene equivalents (see Table 9).

Example 2.18: Methyl acrylate homopolymer

1 mmol of (O-ethylxanthyl)malonate (0.28 g) and 40 mmol of methyl acrylate (3.44 g) are introduced
25 into a 10 ml round-bottomed flask containing 4 ml of toluene. The temperature is raised to 80°C and 0.03 mmol of lauroyl peroxide (12.8 mg) are added.

The polymerization lasts 26 hours, during

which 0.02 mmol of lauroyl peroxide are added every two hours.

The polymer is recovered by evaporating, under high vacuum, the toluene and the traces of residual monomer.

It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.19: Styrene homopolymer

10 1 mmol of ethyl α -(O-phenylethyl)-
 α -phenylthiopropionate (0.406 g) and 40 mmol of styrene
(4.16 g) are introduced into a 10 ml round-bottomed
flask. The temperature is raised to 95°C and 0.03 mmol
of lauroyl peroxide (12.8 mg) are added.

15 The polymerization lasts 16 hours, during
which 0.02 mmol of lauroyl peroxide are added every two
hours.

The polymer is recovered by precipitation in
methanol.

20 It is analysed by GPC in THF medium and in
polystyrene equivalents (see Table 9).

Example 2.20: Methyl acrylate homopolymer

1 mmol of ethyl α -(O-phenylethylxanthyl)-
25 α -phenylethanoate (0.36 g) and 40 mmol of methyl
acrylate (3.44 g) are introduced into a 10 ml round-
bottomed flask. The temperature is raised to 80°C and
0.03 mmol of lauroyl peroxide (12.8 mg) are added.

The polymerization lasts 11 hours, during which 0.02 mmol of lauroyl peroxide are added every two hours.

The polymer is recovered by evaporating,
5 under high vacuum, the traces of residual monomer.

It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.21: Methyl acrylate homopolymer

10 1 mmol of (O-ethylxanthyl)isobutyronitrile (0.189 g) and 40 mmol of methyl acrylate (3.44 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 80°C and 0.03 mmol of lauroyl peroxide (12.8 mg) are added.

15 The polymerization lasts 6 hours, during which 0.02 mmol of lauroyl peroxide are added every two hours, after 2 and 4 hours.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomers.

20 It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.22: Methyl acrylate homopolymer

1 mmol of ethyl (O-neopentylxanthyl)malonate
25 (0.322 g) and 40 mmol of methyl acrylate (3.44 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 80°C and 0.03 mmol of lauroyl peroxide (12.8 mg) are added.

The polymerization lasts 4 hours, during which 0.02 mmol of lauroyl peroxide are added after two hours.

The polymer is recovered by evaporating,
5 under high vacuum, the traces of residual monomer.

It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.23: Methyl acrylate homopolymer

10 1 mmol of ethyl (O-isobornylxanthyl)malonate (0.388 g) and 40 mmol of methyl acrylate (3.44 g) are added to a 10 ml round-bottomed flask. The temperature is raised to 80°C and 0.03 mmol of lauroyl peroxide (12.8 mg) are added.

15 The polymerization lasts 2 hours 30 minutes during which 0.02 mmol of lauroyl peroxide are added after 2 hours.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomer.

20 It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.24: Vinyl acetate homopolymer

1 mmol of ethyl (O-isobornyl)malonate
25 (0.388 g) and 77 mmol of vinyl acetate (6.62 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 70°C and 0.01 mmol of AIBN (azobisisobutyronitrile) (1.64 mg) are added. The

polymerization lasts 24 hours, during which several additions of AIBN are made:

- 1.4 mg after two hours,
- 2.2 mg after four hours.

5 The polymer is recovered by evaporating, under high vacuum, the traces of residual monomers.

 It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

10 **Example 2.25: Acrylic acid homopolymers**

 25 g of acrylic acid are dissolved in 85 g of water and then the solution thus obtained is neutralized to a pH between 6 and 7: this solution is solution 1.

15 0.35 g of 2,2'-azobis(2-methylpropionamide)-dihydrochloride are dissolved in 150 g of water: this solution is solution 2.

 Into three round-bottomed flasks, each containing a different quantity of (O-isopropylxanthyl)-
20 valeronitrile, are introduced 11 g of solution 1 and 1.5 g of solution 2. The compositions of the various flasks are shown in Table A.

 The temperature is raised to 70°C and polymerization is carried out over 24 hours.

25 The polymer is recovered by evaporating, under high vacuum, the water and the traces of residual monomer.

 It is analysed by GPC in aqueous medium and

in PEO equivalents, the results being given in Table 1.

Table 1

Mass of precursor (g)	Degree of conversion (%)	M_n	PI
0.065	100	14,800	1.7
0.108	100	12,000	1.4
0.163	100	8,900	1.4

Example 2.26: Acrylic acid homopolymer

1 mmol of ethyl α -(O-ethylxanthyl)propionate (0.222 g) and 40 mmol of acrylic acid (2.88 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 80°C and 0.04 mmol of lauroyl peroxide (17 mg) are added.

The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 0.04 mmol after two hours,
- 0.04 mmol after four hours.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomer.

It is analysed by GPC in aqueous medium and in PEO equivalents (see Table 9).

Example 2.27: Acrylic acid homopolymers

Several acrylic acid homopolymers are prepared in the following manner.

5 All the acrylic acid (AA), the AIBN and the ethyl α -(O-ethylxanthyl)propionate precursor are mixed together and introduced into a round-bottomed flask. The amounts are given in Table 2. The temperature is raised to 80°C.

The polymerization lasts 6 hours.

10 The traces of residual monomer are removed by evaporation.

The results, obtained from GPC analysis in THF medium and in polystyrene equivalents, are given in Table 2.

15

Table 2

20

AA mass (g)	AIBN mass (mg)	Precursor mass (g)	M_n	PI
1.53	3.47	0.35	345	1.12
3.39	1.81	0.2	770	1.10
3.85	1.15	0.13	1060	1.25
4.08	0.92	0.10	1290	1.30

Example 2.28: Acrylic acid homopolymers

Several acrylic acid homopolymers are prepared in solution in the following manner.

All the acrylic acid (AA), the AIBN and the ethyl α -(O-ethylxanthyl)propionate precursor are dissolved in acetone in a round-bottomed flask. The respective amounts of each ingredient are given in Table 3.

The temperature is raised to 60°C.

The polymerization lasts 3 hours.

The traces of residual monomer and the solvent are removed by evaporation.

The results, obtained by GPC analysis in THF medium and in polystyrene equivalents, are given in Table 3.

Table 3

AA mass (g)	AIBN mass (mg)	Precursor mass (g)	Volume of solvent (ml)	M_n	PI
5.07	2.93	0.3	8	550	1.10
3.88	1.12	0.12	5	1170	1.19
4.37	0.63	0.07	5	1760	1.29
4.56	0.44	0.05	5	1920	1.27

Example 2.29: Ethyl acrylat homopolymer

The following are introduced into a round-bottomed flask:

- 33.2 mg of ethyl α -(O-ethylxanthyl)propionate (1
5 equivalent),
- 5.01 g of ethyl acrylate (160 equivalents), and
- 8.2 mg of AIBN.

The temperature is raised to 70°C. The polymerization lasts 24 hours.

10 The polymer is recovered by evaporating, under high vacuum, the traces of residual monomer.

It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

15 **Example 2.30: Vinyl acetate homopolymer**

4.3 g of vinyl acetate and 59.7 mg of lauroyl peroxide are introduced into three round-bottomed flasks containing varying amounts of ethyl α -(O-ethylxanthyl)propionate. The temperature is raised
20 to 70°C and the polymerization lasts 6 hours. The amounts of precursor used are given in Table 4.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomer. The results, obtained by GPC analysis in THF medium and in
25 polystyrene equivalents, are given in Table 4.

Table 4

	Mass of precursor (g)	Degree of conversion (%)	M_n	PI
5	0.266	64.4	2100	1.4
	0.130	66.6	4100	1.6
	0.068	66.0	7000	1.9

Example 2.31: Styrene homopolymer obtained in
10 emulsion

The following are introduced into a 1.5 l reactor fitted with a Teflon anchor stirrer:

- 525 g of water,
- 0.2 g of sodium hydrogen carbonate and
- 15 - 10 g of sodium lauryl sulphate.

The temperature is raised to 70°C and 20 g of styrene and all of the ethyl α -(O-ethylxanthyl)propionate precursor are added in one go.

20 Next, the temperature is increased to 85°C and 0.4 g of ammonium persulphate in solution in 16.13 g of water are added in one go.

Styrene (180 g) is then continuously fed in over a period of four hours.

25 The temperature is maintained at 85°C for an additional 2 hours.

The results, obtained from GPC analysis in

THF medium and in polystyrene equivalents, are given in Table 5.

Table 5

5

Mass of precursor (g)	Degree of conversion (%)	M_n	PI
2	88	15,400	1.9
1	90	29,500	1.9

10

Example 2.32: Styrene homopolymer obtained in emulsion

The following are introduced into a 1.5 l reactor fitted with a Teflon anchor stirrer:

- 15
- 475 g of water,
 - 0.2 g of sodium hydrogencarbonate and
 - 10 g of sodium lauryl sulphate.

The temperature is raised to 70°C and the following are added in one go:

- 20
- 20 g of styrene and
 - 2 g of ethyl α -(O-ethylxanthyl)propionate.

Next, the temperature is increased to 85°C and 0.4 g of ammonium persulphate in solution in 16.13 g of water are added in one go.

25 The following are introduced into the reactor, continuously and simultaneously:

- 180 g of styrene over 8 hours,

- 0.4 g of ammonium persulphate in 50.4 g of water over 10 hours.

Specimens are removed regularly and analysed by GPC in THF medium and in polystyrene equivalents.

5 The results obtained are given in Table 6.

Table 6

	Time (h)	Degree of conversion (%)	M_n	PI
10	1	10.1	2500	1.8
	2	18.6	3300	1.8
	4	39.2	6250	1.9
	6	56.3	8100	1.9
	8	73.3	10,000	1.9
15	24	75.7	10,500	1.9

A linear increase in the molecular masses with conversion is observed, thereby demonstrating the controlled character of the radical polymerization.

20

Example 2.33: Ethyl acrylate homopolymer

A solution is prepared which contains:

- 17.64 g of ethyl acrylate;
- 0.459 g of ethyl α -(O-ethylxanthyl)propionate and
- 25 - 0.036 g of AIBN.

1 g of this solution is introduced into 7

tubes which will serve to determine the polymerization kinetics.

These tubes are then heated to 70°C and stopped at different times. For each tube, the polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents.

The results obtained are given in Table 7.

10

Table 7

15

Time (min)	Degree of conversion (%)	M_n	PI
12	0	1900	3.4
21	17	4200	2.5
30	32.3	4300	2.5
42	43.5	4800	2.4
53	46.6	4800	2.5
66	71.4	6700	1.9
124	80.4	7100	1.9

20

A linear increase in the molecular masses with conversion is observed, thereby demonstrating the controlled character of the radical polymerization.

Exempl 2.34: Vinyl acetate homopolymer

A solution is prepared which contains:

- 7.35 g of vinyl acetate,
- 0.229 g of ethyl α -(O-ethylxanthyl)propionate, and
- 5 - 0.018 g of AIBN.

1 g of this solution is introduced into 4 tubes which will serve to determine the polymerization kinetics.

The tubes are then heated to 70°C and stopped
10 at different times. For each tube, the polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents.

The results obtained are given in Table 8.

15

Table 8

Time (min)	Degree of conversion (%)	M_n	PI
12	0		
20 28	13.8	1200	1.4
38	77.8	4300	1.7
51	83.9	4300	1.7

A linear increase in the molecular masses
25 with conversion is observed, thereby demonstrating the controlled character of the radical polymerization.

Results of Examples 2.1 to 2.24, 2.26 and

2.29:

GPC analysis of the homopolymers obtained above is used to measure their number-average mass (M_n).

5 It is also used to measure their weight-average mass (M_w) and hence their polydispersity index (PI) corresponding to the ratio of M_w to M_n .

GPC chromatograms are systematically produced in double detection mode, namely refractometry (RI) and
10 UV absorption (UV). The UV detection wavelength corresponds to the maximum absorption of the xanthate functional group fixed on the end of the chain according to the formula claimed. For all the specimens analysed, there is perfect superposition of the
15 chromatograms obtained from one or other detection mode. This result indicates that the chain ends are functionalized and constitutes an additional proof of the assumed structure of the polymers according to the invention.

20

Table 9

	Examples	Monomer	M_n	PI	Degree of conversion
	Ex. 2.1	styrene	3800	2	
5	Ex. 2.2	styrene	5200	2.1	
	Ex. 2.3	styrene	7900	2.5	
	Ex. 2.4	styrene	3200	1.8	
	Ex. 2.5	styrene	3300	1.9	
	Ex. 2.6	MeA	3500	1.8	
10	Ex. 2.7	MeA	3750	1.7	
	Ex. 2.8	MeA	7300	1.7	
	Ex. 2.9	MeA	3000	1.4	
	Ex. 2.10	EtA	3700	1.6	
	Ex. 2.11	MeA	3500	1.35	
15	Ex. 2.12	2EHA	6900	1.5	
	Ex. 2.13	MVA	3200	1.35	
	Ex. 2.14	MVA	2100	1.18	
	Ex. 2.15	styrene	6200	2	
	Ex. 2.16	styrene	3800	1.6	
20	Ex. 2.17	styrene	4300	1.9	78
	Ex. 2.18	MeA	3900	1.5	95
	Ex. 2.19	styrene	3400	1.8	77
	Ex. 2.20	MeA	3100	1.6	60
	Ex. 2.21	MeA	3600	1.4	75
25	Ex. 2.22	MeA	5100	1.4	90
	Ex. 2.23	MeA	4000	1.7	88
	Ex. 2.24	MVA ?	2500	1.8	29
	Ex. 2.26	AA	6600	2.3	97
30	Ex. 2.29	EtA	29,400	1.9	93

Example 2.35: Vinyl acetate homopolymer

The following are introduced into a 10 ml round-bottomed flask:

- 0.899 g of vinyl acetate (i.e. approximately 10 equivalents),
- 0.220 g of ethyl α -(O-ethylxanthylpropionate (1 equivalent), and
- 17.2 mg of AIBN.

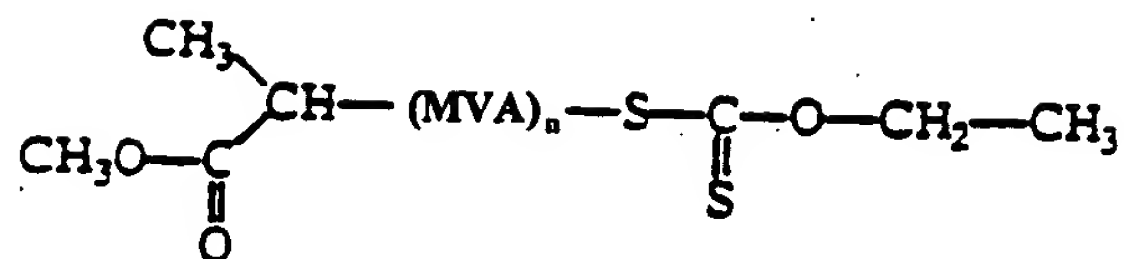
The temperature is raised to 70°C. The polymerization lasts 24 hours.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomer and is analysed by MALDI-TOF on a DHB matrix. The results are given in Table 10.

Table 10

Number of MVA units	Theoretical mass (g)	MALDI-TOF mass (g)
7	833	831.556
8	919	917.458
9	1005	1003.638

In Table 10, the theoretical masses are calculated assuming a structure according to the formula:



5 It is necessary to add 23 g to the mass
 obtained since the species detected are in sodium salt
 form. The excellent agreement between the theoretical
 masses and the masses measured by MALDI-TOF confirm the
 assumed mechanism for the polymerization and the
 10 structure of the polymers obtained.

EXAMPLES 3 - SYNTHESSES OF BLOCK COPOLYMERS

Example 3.1: p(MeA-b-St) block copolymer

15 The following are introduced into a 10 ml
 round-bottomed flask:

- 1 mmol of ethyl α -(O-ethylxanthyl)propionate
 (0.222 g) and
- 20 mmol of methyl acrylate (1.72 g).

20 The mixture is heated to 80°C and 0.02 mmol
 of lauroyl peroxide (8.52 mg) are added. The mixture is
 maintained at temperature for 45 min after which it
 coagulates. Next, the reaction mixture is dissolved in
 3 ml of toluene and then evaporated to dryness, in
 25 vacuo. This operation is repeated three times in order
 to remove the traces of residual methyl acrylate. This
 synthesis results in a precursor which can be used for
 preparing a block copolymer.

Next, 20 mmol of styrene (2.08 g) are introduced into the reactor. The temperature is raised to 110°C and 0.02 mmol of lauroyl peroxide (8.52 mg) are added. This second step lasts 6 hours, during which
5 several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours.

The copolymer obtained is recovered by precipitation in methanol and analysed by double
10 detection GPC - refractometry and UV spectrometry. The GPC solvent is THF and the masses are given in polystyrene equivalents. The results are given in Table 12.

15 **Example 3.2: p(St-b-MeA) block copolymer**

The following are introduced into a 10 ml round-bottomed flask:

- 1 mmol of ethyl α -(O-ethylxanthyl)propionate (0.222 g),
- 20 - 20 mmol of styrene (2.08 g), and
- 1 ml of toluene.

The reaction mixture is raised to 110°C and 0.025 mmol of lauroyl peroxide (10.6 mg) are introduced into the reactor. This first step lasts 9 hours, during
25 which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,

- 0.01 mmol after eight hours.

Next, the mixture is cooled to 80°C and the following are introduced:

- 20 mmol of methyl acrylate (1.72 g) and
- 5 - 0.03 mmol of lauroyl peroxide (12.8 mg).

This second step lasts 7 hours, during which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 10 - 0.01 mmol after six hours.

The polymer obtained is recovered and analysed as in Example 3.1. The results are given in Table 11.

15 **Example 3.3: p(St-b-MeA) block copolymer**

The following are introduced into a 10 ml round-bottomed flask:

- 1 mmol of [1-(O-ethylxanthyl)ethyl]benzene (0.226 g)
- and
- 20 - 20 mmol of styrene (2.08 g).

The temperature is raised to 90°C and 0.03 mmol of lauroyl peroxide (12.8 mg) are added. The temperature is maintained at 90°C for 10 hours, during which several additions of initiator are made:

- 25 - 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,
- 0.01 mmol after eight hours.

Next, the reaction mixture is cooled to 80°C and the following are introduced:

- 20 mmol of methyl acrylate (1.72 g) and
- 0.02 mmol of lauroyl peroxide (8.52 mg).

5 This second step lasts 8 hours, during which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,
- 10 - 0.01 mmol after seven hours.

The polymer obtained is recovered and analysed as in Example 3.1. The results are given in Table 12.

15 **Example 3.4: p(St-b-MeA-b-St) block copolymer**

The following are introduced into a 10 ml round-bottomed flask:

- 1 mmol of [1-(O-ethylxanthyl)ethyl]benzene (0.226 g)
- and
- 20 - 20 mmol of styrene (2.08 g).

The temperature is raised to 90°C and 0.03 mmol of lauroyl peroxide (12.8 mg) are added. The temperature is maintained at 90°C for 10 hours, during which several additions of initiator are made:

- 25 - 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,
- 0.01 mmol after eight hours.

Next, the reaction mixture is cooled to 80°C and the following are introduced:

- 20 mmol of methyl acrylate and
- 0.02 mmol of lauroyl peroxide.

5 This second step lasts 8 hours, during which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,
- 10 - 0.01 mmol after seven hours.

The temperature is again raised to 90°C and the following are introduced:

- 20 mmol of styrene (2.08 g) and
- 0.02 mmol of lauroyl peroxide.

15 This third step lasts 8 hours, during which several additions of initiator are made:

- 1 mmol after two hours,
- 1 mmol after four hours,
- 1 mmol after six hours.

20 The polymer obtained is recovered and analysed as in Example 3.1. The results are given in Table 12.

Example 3.5: p(MeA-b-St) block copolymer

25 The following are introduced into a round-bottomed flask:

- 1 mmol of [1-(O-ethylxanthyl)ethyl]benzene (0.226 g)
- and

- 20 mmol of methyl acrylate (1.72 g).

The temperature is raised to 80°C and 0.02 mmol of lauroyl peroxide are added. This first step lasts 8 hours, during which several additions of initiator are made:

- 1 mmol after two hours,
- 1 mmol after four hours,
- 1 mmol after six hours.

Next, the temperature is increased to 90°C and the following are introduced:

- 20 mmol of styrene and
- 0.02 mmol of lauroyl peroxide. This second step lasts 14 hours, during which several additions of initiator are made:
- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,
- 0.01 mmol after eight hours,
- 0.01 mmol after ten hours,
- 0.01 mmol after twelve hours.

The polymer obtained is recovered and analysed as in Example 3.1. The results are given in Table 12.

Example 3.6: p(EtA-b-MVA) block copolymer

The following are introduced into a round-bottomed flask:

- 1.881 g of ethyl acrylate,

- 0.111 g of ethyl α -(O-ethylxanthyl)propionate and
- 8.6 mg of lauroyl peroxide.

The temperature is raised to 80°C. The polymerization lasts 6 hours, during which several
5 additions of lauroyl peroxide are made:

- 9.2 mg after 2 hours,
- 9.0 mg after 4 hours.

After cooling, the traces of residual ethyl acrylate are removed by evaporation under high vacuum
10 and a small fraction of the polymer is taken for GPC analysis in THF medium and in polystyrene equivalents. The results are as follows:

- degree of conversion: 98.3%
- $M_n = 2800$
- 15 - $PI = 1.8$.

Next, 1.853 g of vinyl acetate and 8.6 mg of lauroyl peroxide are introduced into the flask. The temperature is raised to 80°C. The polymerization lasts 6 hours, during which several additions of lauroyl
20 peroxide are made:

- 8.6 mg after 2 hours,
- 8.5 mg after 4 hours.

The traces of residual vinyl acetate are removed by evaporation under high vacuum. The results
25 are given in Table 12.

Example 3.7: p(EtA-b-tBuA) block copolymer

The following are introduced into a round-

bottomed flask:

- 1.881 g of ethyl acrylate,
- 0.111 g of ethyl α -(O-ethylxanthyl)propionate and
- 9.0 mg of lauroyl peroxide. The temperature is raised
- 5 to 80°C. The polymerization lasts 6 hours, during
- which several additions of lauroyl peroxide are made:
- 8.6 mg after 2 hours,
- 8.9 mg after 4 hours.

After cooling, the traces of residual ethyl

10 acrylate are removed by evaporation under high vacuum

and a small fraction of the polymer is taken to be

analysed by GPC in THF medium and in polystyrene

equivalents:

- degree of conversion: 98.6%
- 15 - $M_n = 2600$
- $PI = 1.9$.

Next, the following are introduced into the

flask:

- 2.7467 g of tert-butyl acrylate and
- 20 - 8.5 mg of lauroyl peroxide.

The temperature is raised to 80°C. The

polymerization lasts 6 hours, during which several

additions of lauroyl peroxide are made:

- 8.7 mg after 2 hours,
- 25 - 8.5 mg after 4 hours.

The traces of residual tert-butyl acrylate

are removed by evaporation under high vacuum and the

copolymer obtained is analysed by GPC in THF medium and

in polystyrene equivalents. The results are given in Table 12.

Example 3.8: p(t-BuA-b-MVA) block copolymer

5 The following are introduced into a round-bottomed flask:

- 2.737 g of tert-butyl acrylate,
- 0.111 g of ethyl α -(O-ethylxanthyl)propionate and
- 8.7 mg of lauroyl peroxide.

10 The temperature is raised to 80°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 8.9 mg after 2 hours,
- 8.9 mg after 4 hours.

15 After cooling, the residual traces of tert-butyl acrylate are removed by evaporation under high vacuum and a small fraction of the polymer is taken to be analysed by GPC in THF medium and in polystyrene equivalents:

- 20 - degree of conversion: 98.3%,
- $M_n = 2500$,
 - $PI = 2.4$.

 Next, the following are introduced into the flask:

- 25 - 1.851 g of vinyl acetate and
- 8.5 mg of lauroyl peroxide.

 The temperature is raised to 80°C. The polymerization lasts 6 hours, during which several

additions of lauroyl peroxide are made:

- 8.7 mg after 2 hours,
- 8.5 mg after 4 hours.

The traces of residual vinyl acetate are removed by evaporation under high vacuum and the copolymer obtained is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in Table 12.

10 **Example 3.9: p(tBuA-b-EtA) block copolymer**

The following are introduced into a round-bottomed flask:

- 2.737 g of tert-butyl acrylate,
- 0.111 g of ethyl -(O-ethylxanthyl)propionate and
- 15 - 8.4 mg of lauroyl peroxide.

The temperature is raised to 80°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 9.0 mg after 2 hours,
- 20 - 8.7 mg after 4 hours.

After cooling, the residual traces of tert-butyl acrylate are removed by evaporation under high vacuum and a small fraction of the polymer is taken to be analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 98.1%,
- $M_n = 2500$,
- PI = 2.5.

Next, the following are introduced into the flask:

- 1.896 g of ethyl acrylate and
- 8.8 mg of lauroyl peroxide.

5 The temperature is raised to 80°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 8.7 mg after 2 hours,
- 8.5 mg after 4 hours.

10 The traces of residual ethyl acrylate are removed by evaporation under high vacuum and the copolymer obtained is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in Table 12.

15

Example 3.10: p(EtA-b-St) block copolymer

The following are introduced into a round-bottomed flask:

- 1.881 g of ethyl acrylate,
- 20 - 0.111 g of ethyl α -(O-ethylxanthyl)propionate and
- 8.8 mg of lauroyl peroxide.

The temperature is raised to 80°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 25 - 9.0 mg after 2 hours,
- 8.5 mg after 4 hours.

After cooling, the residual traces of ethyl acrylate are removed by evaporation under high vacuum

and a small fraction of the polymer is taken to be analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 97.5%,
- 5 - $M_n = 3000$,
- $PI = 1.8$.

Next, the following are introduced into the flask:

- 2.231 g of styrene and
- 10 - 9.0 mg of lauroyl peroxide.

The temperature is raised to 115°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 8.7 mg after 2 hours,
- 15 - 9.9 mg after 4 hours.

The traces of residual styrene are removed by evaporation under high vacuum and the copolymer obtained is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in Table

20 12.

Example 3.11: p(tBuA-b-St) block copolymer

The following are introduced into a round-bottomed flask:

- 25 - 2.737 g of tert-butyl acrylate,
- 0.111 g of ethyl α -(O-ethylxanthyl)propionate and
- 9.0 mg of lauroyl peroxide.

The temperature is raised to 80°C. The

polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 8.5 mg after 2 hours,
- 9.6 mg after 4 hours.

5 After cooling, the residual traces of tert-butyl acrylate are removed by evaporation under high vacuum and a small fraction of the polymer is taken to be analysed by GPC in THF medium and in polystyrene equivalents:

- 10 - degree of conversion: 98.4%,
 - $M_n = 2800$,
 - $PI = 2.4$.

Next, the following are introduced into the flask:

- 15 - 2.246 g of styrene and
 - 8.4 mg of lauroyl peroxide.

The temperature is raised to 115°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 20 - 9.2 mg after 2 hours,
 - 9.2 mg after 4 hours.

The traces of residual styrene are removed by evaporation under high vacuum and the copolymer obtained is analysed by GPC in THF medium and in
25 polystyrene equivalents. The results are given in Table 12.

Example 3.12: p(EtA-b-tBuA-b-St) block copolymer

The following are introduced into a round-bottomed flask:

- 5 - 2.248 g of styrene,
- the entire copolymer obtained in Example 3.7 and
- 8.3 mg of lauroyl peroxide.

The temperature is raised to 115°C. The polymerization lasts 6 hours, during which several

10 additions of lauroyl peroxide are made:

- 9.0 mg after 2 hours,
- 8.5 mg after 4 hours.

The traces of residual styrene are removed by evaporation under high vacuum and the copolymer obtained

15 is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in Table 12.

Example 3.13: p(St-b-EtA) block copolymer

The following are introduced into a round-bottomed flask:

20

- 2.224 g of styrene,
- 0.111 g of ethyl α -(O-ethylxanthyl)propionate and
- 8.6 mg of lauroyl peroxide.

The temperature is raised to 115°C. The polymerization lasts 6 hours, during which several

25 additions of lauroyl peroxide are made:

- 8.7 mg after 2 hours,
- 8.3 mg after 4 hours.

After cooling, the traces of residual styrene are removed by evaporation under high vacuum and a small fraction of the polymer is taken to be analysed by GPC in THF medium and in polystyrene equivalents:

- 5 - degree of conversion: 98.0%
 - $M_n = 3500$,
 - $PI = 2.2$.

Next, the following are introduced into the flask:

- 10 - 2 ml. of toluene,
 - 1.892 g of ethyl acrylate and
 - 8.5 mg of lauroyl peroxide.

The temperature is raised to 80°C. The polymerization lasts 6 hours, during which several
 15 additions of lauroyl peroxide are made:

- 9.4 mg after 2 hours,
 - 9.2 mg after 4 hours.

The traces of residual ethyl acrylate are removed by evaporation under high vacuum and the
 20 copolymer obtained is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in table 12.

Example 3.14: p(St-b-tBuA) block copolymer

25 The following are introduced into a round-bottomed flask:

- 2.224 g of styrene,
 - 0.111 g of ethyl α -(O-ethylxanthyl)propionate and

- 8.6 mg of lauroyl peroxide.

The temperature is raised to 115°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 5 - 8.7 mg after 2 hours,
- 9.5 mg after 4 hours.

After cooling, the traces of residual styrene are removed by evaporation under high vacuum and a small fraction of the polymer is taken to be analysed
10 by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 97.2%
- M_n = 3400,
- PI = 2.2.

Next, the following are introduced into the
15 flask:

- 2 ml of toluene,
- 2.747 g of tert-butyl acrylate and
- 9.3 mg of lauroyl peroxide.

The temperature is raised to 80°C. The
20 polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 8.7 mg after 2 hours,
- 9.3 mg after 4 hours.

The traces of residual tert-butyl acrylate
25 are removed by evaporation under high vacuum and the copolymer obtained is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in table 12.

Example 3.15: p(tBuA-b-EtA-b-St) block**copolymer**

The following are introduced into a round-bottomed flask:

- 5 - 2 ml of toluene,
- 2.229 g of styrene,
- the entire copolymer obtained in Example 3.9 and
- 9.1 mg of lauroyl peroxide.

The temperature is raised to 120°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 8.5 mg after 2 hours,
- 8.5 mg after 4 hours.

The traces of residual styrene are removed by evaporation under high vacuum and the copolymer obtained is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in Table 12.

Example 3.16: pBuA-b-PVA block copolymers

(PVA: polyvinyl alcohol)

These copolymers are obtained by hydrolysing their p(BuA-b-MVA) equivalents.

A series of p(BuA-b-MVA) block copolymers is prepared. All the copolymers are obtained according to the following general operating method.

The following are introduced into a round-bottomed flask:

- butyl acrylate (BuA),

- ethyl α -(O-ethylxanthyl)propionate and
- approximately one third of the total amount of lauroyl peroxide necessary for this first step.

The temperature is raised to 80°C. The polymerization lasts 6 hours, during which two additions of initiator are made after 2 and 4 hours. Each of the additions corresponds to approximately one third of the total amount of lauroyl peroxide of the first step.

10 The traces of residual butyl acrylate are removed by evaporation and a small fraction of the polymer is taken to be analysed.

- Next, the following are added to the flask:
- vinyl acetate and
 - 15 - approximately one third of the total amount of lauroyl peroxide necessary for this second step.

The temperature is again raised to 80°C. The polymerization lasts 6 hours and the rest of the initiator is added in the same way as for the synthesis of the first block. The block copolymer is recovered after evaporating the traces of residual vinyl acetate and analysed by GPC in THF medium and in polystyrene equivalents.

20 The amounts of ingredients used for each of the copolymers, as well as the results obtained, are given in Table 11.

Table 11

	Polymerization 1			Homopolymer		Polymerization 2		Block polymer	
	BuA mass (g)	Precursor mass (g)	Perox. mass (mg)	M_n	PI	MVA mass (g)	Perox. mass (mg)	M_n	PI
5	13.713	1.126	0.257	2500	1.6	13.789	0.263	4500	1.4
	13.695	1.125	0.257	2500	1.6	18.395	0.265	5300	1.4
10	19.158	0.791	0.347	3900	2.0	6.461	0.350	5600	1.7
	19.157	0.798	0.360	3900	2.0	12.872	0.352	7200	1.6
	19.242	1.568	0.370	2500	1.6	6.470	0.365	3200	1.5
	19.295	1.568	0.371	2500	1.7	12.969	0.359	4100	1.4
15	6.71	1.067	0.246	1500	1.4	22.027	0.497	5900	1.5

Next, the block polymers obtained are hydrolysed: they are dissolved in methanol, with 50% solids content, and then a catalytic amount of sodium hydroxide is added and the reaction mixture is heated at 60°C for 1 hour.

The pBuA-b-PVA copolymers are recovered by evaporating the methanol.

Example 3.17: pAA-b-PVA block copolymer

This copolymer is obtained by hydrolysing the corresponding p(tBuA-b-MVA) copolymer.

The following are introduced into a round-bottomed flask:

- 2.737 g of tert-butyl acrylate,
- 0.111 g of ethyl α -(O-ethylxanthyl)propionate and
- 5 - 8.5 mg of lauroyl peroxide.

The temperature is raised to 80°C.

The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 9.5 mg after 2 hours,
- 10 - 9.8 mg after 4 hours.

After cooling, the traces of residual tert-butyl acrylate are removed by evaporation under high vacuum.

A small fraction of the polymer is taken to be analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 99.0%,
- $M_n = 4300$,
- $PI = 1.7$.

20 Next, the following are introduced into the flask:

- 1.831 g of vinyl acetate and
- 8.6 mg of lauroyl peroxide.

The temperature is raised to 80°C.

25 The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 9.2 mg after 2 hours,
- 9.2 mg after 4 hours.

The traces of residual vinyl acetate are removed by evaporation under high vacuum and the copolymer obtained is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in

5 Table 12.

Next, the copolymer obtained is hydrolysed in the following manner.

The copolymer is introduced into a water/methanol (10 ml/4 ml) mixture. Three drops of 95%
10 sulphuric acid are added so as to obtain a pH of 1. The temperature is raised to 70°C. After 2 hours 15 minutes, 8 ml of methanol are added and, after 5 hours, three new drops of 95% sulphuric acid are added. This first step lasts 24 hours and enables the poly(tert-butyl acrylate)
15 block to be converted into polyacrylic acid.

Next, the temperature is returned to room temperature and the solvent (water + methanol) is removed by evaporation. The dry residue obtained is redissolved in 30 ml of methanol and a catalytic amount
20 of NaOH is added. The temperature is again raised to 70°C, at which it is maintained for 24 hours.

The polyacrylic acid/polyvinyl alcohol copolymer obtained is recovered by evaporating the methanol.

25

Example 3.18: p(BuA-b-EtA) block copolymer

The following are introduced into a reactor fitted with a stirring system:

- 60 g of isopropyl acetate,
- 90 g of butyl acrylate and
- 6.9 g of ethyl α -(O-ethylxanthyl)propionate.

The temperature is raised to 80°C. 0.18 g of
5 AIBN in solution in 5 g of isopropyl acetate are added
in one go.

Fifteen minutes later, a solution containing:

- 180 g of isopropyl acetate,
- 274 g of butyl acrylate and
- 10 - 0.5 g of AIBN

is fed continuously over a period of 2 hours.

The temperature and stirring are maintained
for 1 hour 45 minutes after the end of adding the first
monomer.

15 A small fraction of the precursor polymer is
taken and analysed by GPC in THF medium and in
polystyrene equivalents:

- $M_n = 7000$,
- $PI = 1.9$.

20 A second continuous feed then takes place
over a period of 1 hour. It consists of a solution
containing:

- 10 g of isopropyl acetate,
- 163 g of ethyl acrylate and
- 25 - 0.32 g of AIBN.

The temperature and stirring are maintained
for one further hour after the end of adding the second
monomer.

The final copolymer is obtained by evaporating the solvent and the traces of residual monomers and is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in Table 12.

5

Example 3.19: p(BuA-b-EtA) block copolymer

The following are introduced into a reactor fitted with a stirring system:

- 45 g of isopropyl acetate,
- 10 - 75 g of butyl acrylate and
- 6.9 g of ethyl α -(O-ethylxanthyl)propionate.

The temperature is raised to 80°C and 0.15 g of AIBN in solution in 5 g of isopropyl acetate are added in one go.

15

Twenty minutes later, a solution containing:

- 117 g of isopropyl acetate,
- 175 g of butyl acrylate and
- 0.35 g of AIBN

is fed continuously over a period of 1 hour 30 minutes.

20

The temperature and stirring are maintained for 2 hours 10 minutes after the end of adding the first monomer.

25

A small fraction of the precursor polymer is taken and analysed by GPC in THF medium and in polystyrene equivalents:

- $M_n = 5200$
- $PI = 1.8$.

A second continuous feed is then carried out

over a period of 1 hour 40 minutes. It consists of a solution containing:

- 168 g of isopropyl acetate,
- 252 g of ethyl acrylate and
- 5 - 0.5 g of AIBN.

The temperature and stirring are maintained for a further 20 minutes after the end of adding the second monomer.

The final copolymer is recovered by
10 evaporating the solvent and the traces of residual monomers and is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in Table 12.

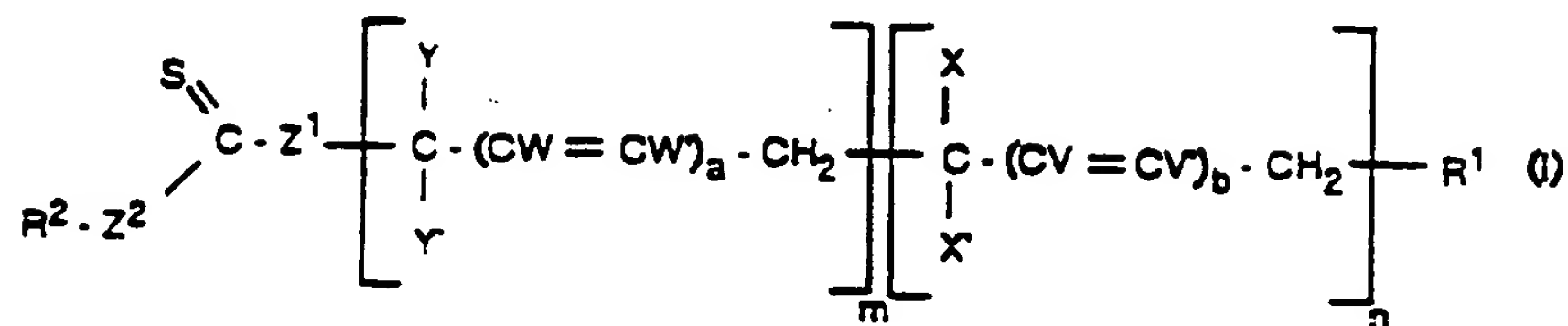
Results of Examples 3.1 to 3.19

Table 12

Examples	Monomers			M_n	PI	Degree of conversion
	M1	M2	M3			
Ex. 3.1	MeA	St	-	4650	1.6	
Ex. 3.2	St	MeA	-	4300	1.7	
Ex. 3.3	St	MeA	-	4200	1.8	
Ex. 3.4	St	MeA	St	6200	2	
Ex. 3.5	MeA	St	-	3750	1.8	
Ex. 3.6	EtA	MVA	-	5600	1.4	92.3%
Ex. 3.7	EtA	tBuA	-	6800	1.7	97.8%
Ex. 3.8	tBuA	MVA	-	6900	1.5	83.8%
Ex. 3.9	tBuA	EtA	-	7000	2.0	96.1%
Ex. 3.10	EtA	St	-	7600	1.8	98.4%
Ex. 3.11	tBuA	St	-	8100	2.9	95.9%
Ex. 3.12	EtA	tBuA	St	13,000	2.4	97.5%
Ex. 3.13	St	EtA	-	6200	1.9	> 99%
Ex. 3.14	St	tBuA	-	7100	1.9	> 99%
Ex. 3.15	tBuA	EtA	St	11,400	2.4	> 99%
Ex. 3.17	tBuA	MVA	-	7400	1.4	88%
Ex. 3.18	BuA	EtA	-	8700	2.2	95%
Ex. 3.19	Bua	EtA	-	10,000	2.0	80%

CLAIMS

1. Process for preparing block polymers of general formula (I):



5 in which:

- $Z^1 = S$ or P ,

- $Z^2 = O$, S or P ,

- R^1 and R^2 , which are identical or different, represent:

10 . an optionally substituted alkyl, acyl, aryl, alkene or alkyne group (i),

or

. an optionally substituted, saturated or unsaturated, carbon or aromatic ring (ii),

or

15 . an optionally substituted, saturated or unsaturated heterocycle (iii),

it being possible for these groups and rings (i),

(ii) and (iii) to be substituted with substituted

phenyl groups, substituted aromatic groups, or

20 groups: alkoxycarbonyl or aryloxycarbonyl ($-COOR$),

carboxy ($-COOH$), acyloxy ($-O_2CR$), carbamoyl ($-CONR_2$),

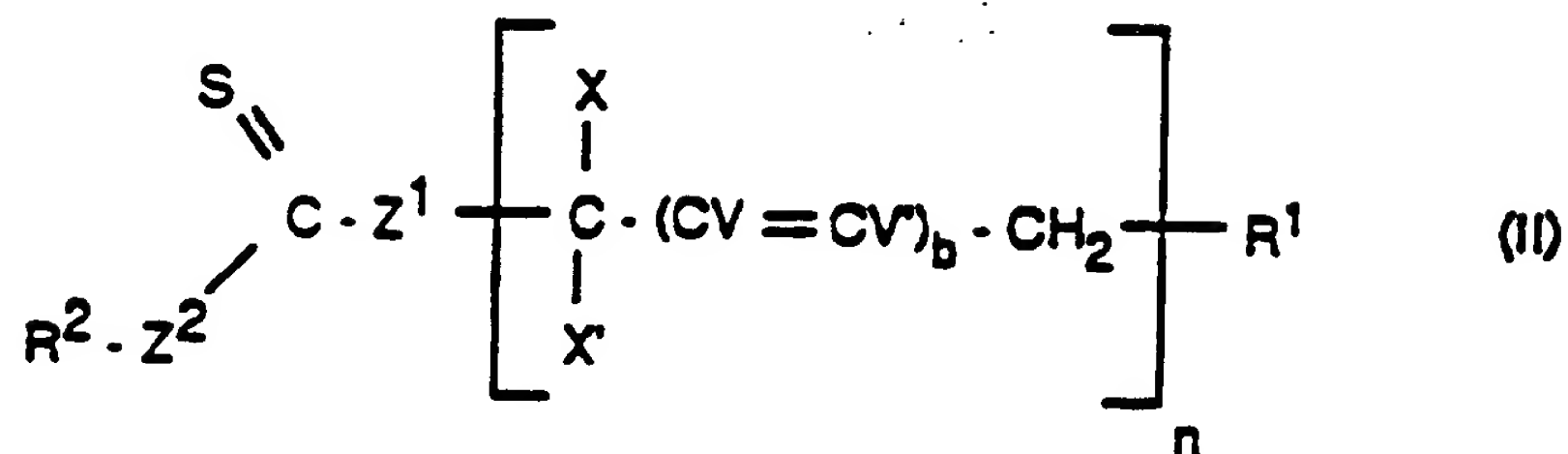
cyano ($-CN$), alkylcarbonyl, alkylarylcarbonyl,

arylcarbonyl, arylalkylcarbonyl, phthalimido,

maleimido, succinimido, amidino, guanidino, hydroxyl

- (-OH), amino (-NR₂), halogen, allyl, epoxy, alkoxy (-OR), S-alkyl, S-aryl, groups having a hydrophilic or ionic character, such as the alkali metal salts of carboxylic acids, the alkali metal salts of sulphonic acid, polyalkylene oxide chains (PEO, PPO), cationic substituents (quaternary ammonium salts),
- 5 R representing an alkyl or aryl group,
 . a polymer chain,
- V, V', W and W', which are identical or different,
 10 represent: H, an alkyl group or a halogen,
- X, X', Y and Y', which are identical or different,
 represent H, a halogen or an R³, OR³, O₂COR³, NHCOH, OH, NH₂, NHR³, N(R³)₂, (R³)₂N⁺O⁻, NHCOR³, CO₂H, CO₂R³, CN, CONH₂, CONHR³ or CONR³₂ group, in which R³ is chosen
 15 from alkyl, aryl, aralkyl, alkaryl, alkene or organosilyl groups, optionally perfluorinated and optionally substituted with one or more carboxyl, epoxy, hydroxyl, alkoxy, amino, halogen or sulphonic groups,
- a and b, which are identical or different, are equal
 20 to 0 or 1,
- m and n, which are identical or different, are greater than or equal to 1 and, when one or other is greater than 1, the individual repeat units are identical or different,
- 25 in which process the following are brought into contact with each other:
- an ethylenically unsaturated monomer of formula:
 $CYY' (=CW-CW')_a=CH_2,$

- a precursor compound of general formula (II):



- a radical polymerization initiator.

2. Process according to claim 1, characterized in that the ethylenically unsaturated monomer is
5 chosen from: styrene or its derivatives, butadiene, chloroprene, (meth)acrylic esters, and vinylnitriles.

3. Process according to the preceding claim, characterized in that the ethylenically unsaturated monomer is chosen from vinylacetate,
10 vinylversatate and vinylpropionate.

4. Process according to any one of the preceding claims, characterized in that R^1 represents:

- a group of formula $\text{CR}'^1\text{R}'^2\text{R}'^3$, in which:

15 . R'^1 , R'^2 and R'^3 represent groups (i), (ii) or (iii) as defined above, or

. $\text{R}'^1 = \text{R}'^2 = \text{H}$ and R'^3 is an aryl, alkene or alkyne group,

- or a $-\text{COR}'^4$ group in which R'^4 represents a group (i), (ii) or (iii).

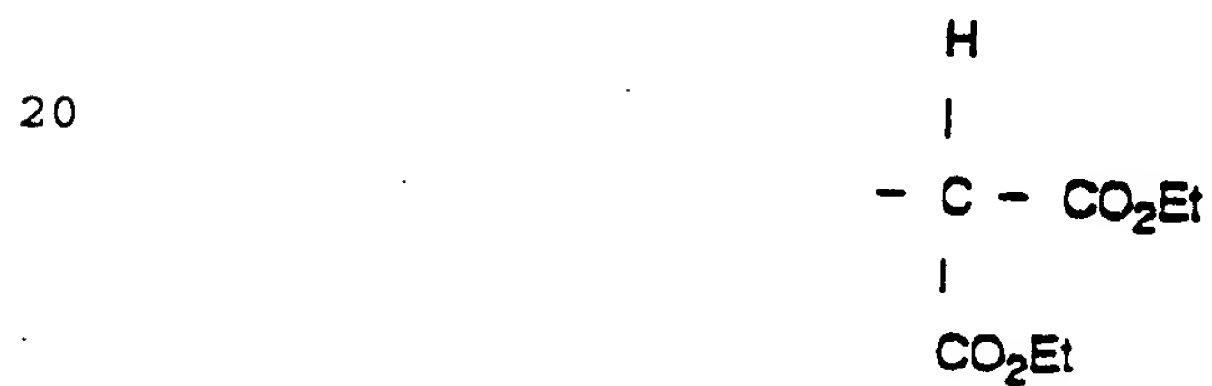
20 5. Process according to any one of the preceding claims, characterized in that R^2 represents a group of formula: $-\text{CH}_2\text{R}'^5$, in which R'^5 represents H or

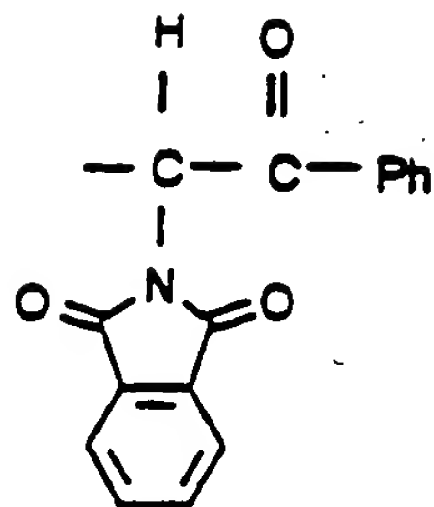
a group (i), (ii) or (iii) with the exception of aryl, alkyne and alkene groups.

6. Process according to one of the preceding claims, characterized in that Z^1 is a sulphur atom and Z^2 is an oxygen atom.

7. Process according to the preceding claim, characterized in that:

- R^1 is chosen from the groups:





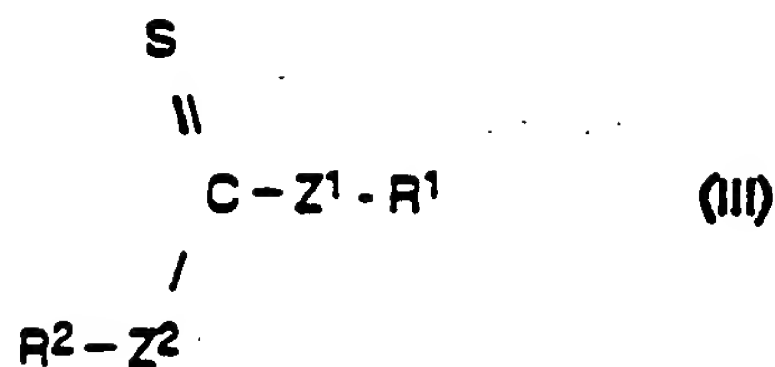
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- and R^2 is an ethyl or phenyl group.

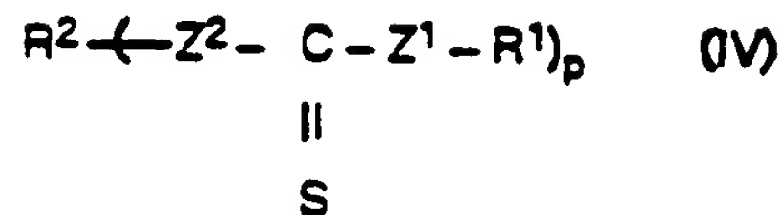
8. Process according to one of the preceding claims, characterized in that the compounds
 10 (II) are chosen from styrene ($Y' = \text{H}$, $Y = \text{C}_6\text{H}_5$, $b = 0$), methyl acrylate ($Y' = \text{H}$, $Y = \text{COOMe}$, $b = 0$), ethyl acrylate ($Y' = \text{H}$, $Y = \text{COOEt}$, $b = 0$), butyl acrylate ($Y' = \text{H}$, $Y = \text{COOBu}$, $b = 0$), tert-butyl acrylate ($Y' = \text{H}$, $Y = \text{COOtBu}$, $b = 0$), vinyl acetate ($Y' = \text{H}$, $Y = \text{OCOMe}$, $b = 0$) and acrylic acid ($Y' = \text{H}$, $Y = \text{COOH}$, $b = 0$) homopolymers, for which:

- $Z^1 = \text{S}$, $Z^2 = \text{O}$, $R^1 = \text{CHCH}_3(\text{CO}_2\text{Et})$ and $R^2 = \text{Et}$, or
- $Z^1 = \text{S}$, $Z^2 = \text{O}$, $R^1 = \text{CH}(\text{CO}_2\text{Et})_2$ and $R^2 = \text{Et}$.

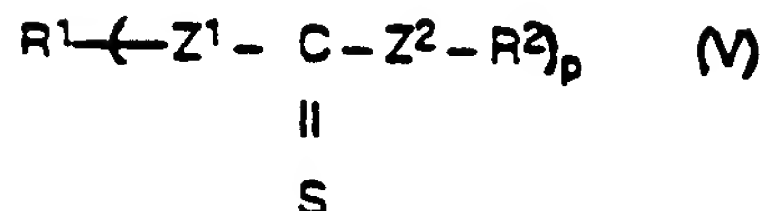
9. Process according to any one of the preceding claims, characterized in that the precursor
 20 compound of general formula (II) is a polymer and in that the said polymer comes from the radical polymerization of an ethylenically unsaturated monomer of formula: $\text{CXX}'(=\text{CV}-\text{CV}')_b=\text{CH}_2$, during which
 25 polymerization the said monomer is brought into contact with a radical polymerization initiator and a compound of general formula (III), (IV) or (V):



5



10



p being between 2 and 10.

10. Process according to the preceding claim, characterized in that the compound (III) is
 15 chosen from ethyl- α -(O-ethylxanthyl)propionate ($\text{Z}^1 = \text{S}$, $\text{Z}^2 = \text{O}$, $\text{R}^1 = \text{CH}(\text{CH}_3)(\text{CO}_2\text{Et})$, $\text{R}^2 = \text{Et}$) and [1-(O-ethylxanthyl)malonate ($\text{Z}^1 = \text{S}$, $\text{Z}^2 = \text{O}$, $\text{R}^1 = \text{CH}(\text{CO}_2\text{Et})_2$, $\text{R}^2 = \text{Et}$).

11. Process for preparing block polymers,
 20 characterized in that the implementation of the process according to one of claims 1 to 10 is repeated at least once, using:

- different monomers from those in the previous implementation, and
- 25 - instead of the precursor compound of formula (II), the block polymer coming from the previous implementation.

12. Block polymer which can be obtained by

the process according to one of claims 1 to 10 or 11.

13. Block polymer according to the preceding claim, characterized in that it has a polydispersity index of at most 2.

5 14. Block polymer according to claim 12 or 13, characterized in that it has a polydispersity index of at most 1.5.

10 15. Block polymer according to any one of claims 12 to 14, characterized in that it is of general formula (I) in which Z^1 is a sulphur atom and Z^2 is an oxygen atom.

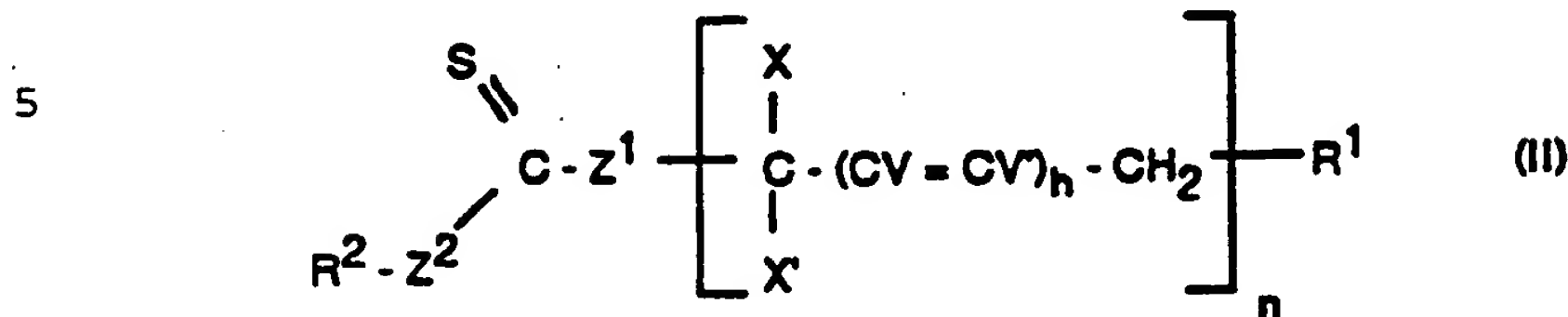
15 16. Block polymer according to any one of claims 12 to 15, characterized in that they have at least two polymer blocks chosen from the following combinations:

- polystyrene/polymethyl acrylate
- polystyrene/polyethyl acrylate,
- polystyrene/poly(*tert*-butyl acrylate),
- polyethyl acrylate/polyvinyl acetate,
- 20 - polybutyl acrylate/polyvinyl acetate,
- polyethyl acrylate/poly(*tert*-butyl acrylate),
- poly(*tert*-butyl acrylate)/polyvinyl acetate,
- polyethyl acrylate/polybutyl acrylate,
- polybutyl acrylate/polyvinyl alcohol,
- 25 - polyacrylic acid/polyvinyl alcohol.

17. Block polymer according to claim 16, characterized in that it is of general formula (I), in which:

- $Z^1 = S$, $Z^2 = O$, $R^1 = CHCH_3(CO_2Et)$ and $R^2 = Et$, or
- $Z^1 = S$, $Z^2 = O$, $R^1 = CH(CO_2Et)_2$ and $R^2 = Et$.

18. Compound of general formula (II):



10 characterized in that it has a polydispersity index of at most 2.

19. Compound of general formula (II) according to the preceding claim, characterized in that it has a polydispersity index of at most 1.5.

20. Compound of general formula (II) according to the preceding claim, characterized in that Z^1 is a sulphur atom, Z^2 is an oxygen atom and n is greater than or equal to 6.

21. Compound of general formula (II) according to Claim 19 or 20, characterized in that it is chosen from styrene ($Y' = H$, $Y = C_6H_5$, $b = 0$), methyl acrylate ($Y' = H$, $Y = COOMe$, $b = 0$), ethyl acrylate ($Y' = H$, $Y = COOEt$, $b = 0$), butyl acrylate ($Y' = H$, $Y = COOBu$, $b = 0$), tert-butyl acrylate ($Y' = H$, $Y = COOtBu$, $b = 0$), vinyl acetate ($Y' = H$, $Y = OCOMe$, $b = 0$) and acrylic acid ($Y' = H$, $Y = COOH$, $b = 0$) polymers, for which:

- $Z^1 = S$, $Z^2 = O$, $R^1 = CH(CH_3)(CO_2Et)$ and $R^2 = Et$, or
- $Z^1 = S$, $Z^2 = O$, $R^1 = CH(CO_2Et)_2$ and $R^2 = Et$.

DATED THIS 23RD DAY OF JUNE 1998


JOHN & KERNICK
FOR THE APPLICANT

